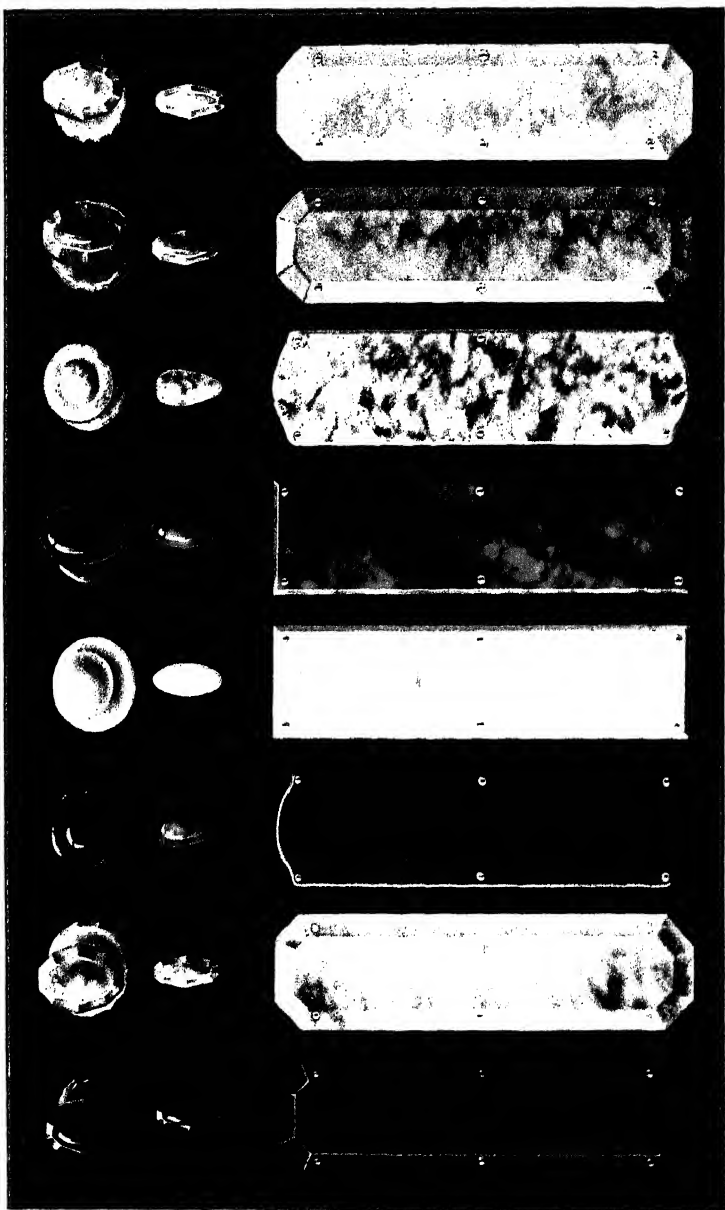


*The British Products Co., Ltd., England*  
**EXAMPLES OF ENGLISH MORTARINGS FROM BRITLE MORTARING POWDERS**



# ARTIFICIAL RESINS

BY  
JOHANNES SCHEIBER

PH.D.  
EXTRAORDINARY PROFESSOR AT THE UNIVERSITY OF LEIPZIG

AND  
KURT SÄNDIG  
PH.D.

*TRANSLATED FROM THE GERMAN BY*  
ERNEST FYLEMAN  
B.Sc., PH.D., F.I.C.



LONDON  
SIR ISAAC PITMAN & SONS, LTD.  
PARKER STREET, KINGSWAY, W.C.2  
BATH, MELBOURNE, TORONTO, NEW YORK

1931





## TRANSLATOR'S PREFACE

THE Artificial Resin industry is a modern development, having started as recently as 1890. The industry was at first confined to the manufacture of substitutes for the various natural resins, already widely used at that time, but with the development of Bakelite, the first hardening resin, in 1907, it reached a new stage by the manufacture of resin-like products possessing valuable hardening properties hitherto unknown. The industry has now attained considerable importance and supplies products which are indispensable for many purposes, for example, for the manufacture of electrical machinery.

It is interesting to observe how the resinous, pitchy products which are the bugbear of the orthodox organic research chemist, and which he is inclined to treat with chilly contempt, have become the basis of an important industry and are deliberately produced by tens of thousands of tons annually, being valuable by the very reason of the non-crystalline and chemically heterogeneous character which provokes the scorn of the contributor to Beilstein. It is perhaps well to be reminded that the ultimate products of chemical industry, those that reach the ultimate consumer, are not usually or very largely pure chemicals of crystalline character, but either structural materials or food products of non-crystalline form.

The present work presents a comprehensive account of the principles underlying the Artificial Resin industry and of their application in practice, which should be of interest to English-speaking readers.

The translator has confined himself to an attempt to reproduce, as accurately as possible, the meaning of the authors.

ERNEST FYLEMAN.



# CONTENTS

	PAGE
PREFACE . . . . .	v
I. INTRODUCTION . . . . .	1
II. THE TYPICAL PROPERTIES OF RESINS . . . . .	13
III. GENERAL CAUSES OF THE EXISTENCE OF RESINS . . . . .	20
IV. SPECIAL CAUSES FOR THE RESINOUS CHARACTER OF DEFINITE MIXTURES . . . . .	30
V. THE RELATIONS BETWEEN RESINOUS CHARACTER AND CHEMICAL CONSTITUTION . . . . .	39
VI. THE LEADING PRINCIPLES OF RESIN PRODUCTION . . . . .	47
VII. SUBDIVISION AND SCOPE OF THE SUBJECT . . . . .	50
VIII. RESIN-FORMING POLYMERIZATION—THEORETICAL . . . . .	52
IX. RESIN-FORMING POLYMERIZATION . . . . .	82
X. RESIN-FORMING CONDENSATIONS . . . . .	133
XI. CUMARONE AND ALDEHYDE RESINS . . . . .	228
XII. PHENOL-ALDEHYDE RESINS . . . . .	272
XIII. UREA-FORMALDEHYDE CONDENSATION PRODUCTS . . . . .	396
APPENDIX . . . . .	411
INDEX . . . . .	443



# ARTIFICIAL RESINS

## CHAPTER I

### INTRODUCTION

THE term "Resin" was originally applied exclusively to a group of natural products. During the last few decennia an increasing number of products have been included in the category of "resins" which are obtained artificially by the systematic exploitation of numerous reactions of organic substances which lead to resinification. The natural and artificial products show no difference with regard to the characteristic properties which endow them with resinic character. Therefore the "artificial resins," "synthetic resins," "resin-like products," and "resin substitutes" (such as shellac and copal substitutes) can be used as perfect substitutes for the natural resins in their industrial applications, such as in the varnish industry, as insulators, as textile dressings, in fireworks, and so forth. These economic possibilities have led to the establishment of a special artificial resin industry, which is steadily growing in importance.

Although the individual chemical constitutions of the various resin products must undoubtedly be of influence (see Chapter V), we must add that close relations between chemical constitution and "resin" characteristics do not exist. It is certain that any such relations are of such a character that they may be fulfilled in very various manners. Otherwise the fact would be unexplainable that great chemical differences exist between the various natural resins, and still more between these and the artificial products. It is true that the opinion has been expressed that certain reactions leading to the production of artificial resins may also have played a part in the formation of natural products.<sup>1</sup> But even should this be so, the exceedingly

<sup>1</sup> See, for example, the articles by A. Michael (*Ber.*, 17 R., 21, 1884), and L. H. Baekeland (*Chem. Ztg.*, 1909, 359), on the natural formation of resins from phenols and aldehydes. Compare also the experiments of O. Doebner on the synthesis of constituents of Guaiacum resin. (*Arch. Pharm.*, 234, 610; C., 1897, I, 167.)

marked variations are very evident. The acceptance of any essential chemical analogies between natural and artificial resins would therefore be more than doubtful.

**The Natural Resins.** These are secretions which are distinguished from vegetable gums and mucilages belonging to the carbohydrate class by their insolubility in water and inability to gelatinize in that liquid, together with the property of solubility in alcohol or ether, although in external appearance they often resemble the former substances closely. Numerous vegetable families produce resinous secretions, including some which are widely distributed, such as the conifers. Some of these families, or at any rate their resin-forming species, are confined to comparatively warm climates, such as the caesalpinioidae, anacardiaceae, burseraceae, umbelliferae, dipterocarpaceae, guttiferae, euphorbiaceae, compositae and so forth.

In many cases such plants are normally provided with resin ducts or cavities, from which the resin flows when open (primary or physiological resin, primary resin flow). More frequently the secretion of resin only occurs under the stimulus of a wound, which may be either natural (animal bites, insect attack, injuries caused by wind, fire, or lightning, and so forth) or artificial (by an axe or knife). In the latter cases the resin secretion is thus a pathological product, and it is of interest to note that when caused in this way the flow of resin is especially copious, a circumstance of great importance in industrial resin production, in which industry "secondary" resin flow is utilized whenever possible. We may add that according to A. Tschirch<sup>1</sup> the production of resinous secretions is always associated with the presence of special "resinogenous" cell layers, which may thus occur not only as normal tissues, but also as pathological formations for the purpose of promoting resin formation in circumstances in which it would not otherwise occur.

The purpose of resin formation is, in every case, the covering of an open wound. In order to facilitate this object such secretions of the living plant are always of a fluid nature and

<sup>1</sup> *Die Harze und die Harzbehälter*, Second Edition; Leipzig, 1906.

## INTRODUCTION

appear at the surface as a liquid, such as turpentine or balsam. On contact with the air, not only do the volatile constituents, consisting of essential oils and terpene hydrocarbons, volatilize, but autoxidation, and so forth, also occur. As a result of these processes the liquid secretion hardens more or less rapidly to a solid resin, which is, however, in the first instance, still soft. Products of this character are known as "recent" resins. In this state all natural resins are easily soluble in alcohols or hydrocarbons, and can therefore be used for the production of varnish.

When resin production is especially copious much of the secretion passes into the soil. This also occurs if the secreting plants are themselves overthrown through the effect of wind, damage, age, floods, and so forth, and are then covered by humus, earth, sand, etc. Such occurrences, which have taken place throughout countless ages, were followed by the gradual decay of the woody material, whilst the resin itself remained intact.

In such cases the processes of evaporation of volatile constituents, autoxidation and polymerization, continued throughout long eras, naturally altered the character of such resins.<sup>1</sup> It is therefore not surprising that the so-called Copals, or "recent fossil resins," in which the phenomena comprised under the name of ripening have acted throughout centuries and possibly throughout thousands of years,<sup>2</sup> are far superior to recent products with regard to mechanical strength and resistance to heat. A further characteristic of these products is a greatly reduced solubility in the solvents commonly used for recent resins.<sup>3</sup> The changes produced by ripening are naturally most strongly developed in resins, the age of which must be reckoned in geological periods. The best known example of

<sup>1</sup> See C. Engler, *Report of the Eighth International Congress of Applied Chemistry*, New York, Vol. 25, 661 (1912).

<sup>2</sup> Kauri pines (*Dammara australis*) attain the age of about 1,000 years, and therefore Kauri resin buried in localities in which the original forests have now disappeared without trace must be several thousand years old. The West African copals found in water-borne secondary deposits, must also be very old.

<sup>3</sup> This is considered to be due to the development of colloidal conditions; see C. Engler and Tausz, *Angew.* 34, 308 (1921).



such "fossil" resins is amber, the matrix of which, the "blue earth" of the Baltic coast, is of oligocene origin. In actual fact, amber (succinite) excels all other known natural resinous products with regard to hardness, strength, and heat resistance; at the same time it is also the least soluble resin known.<sup>1</sup>

The complicated series: fluid secretion → recent resin → recent fossil resin → fossil resin, the chemical relations of which are by no means clear in detail, reminds one, with regard to the associated changes of such physical properties as solubility, hardness, and mechanical strength, of the changes which occur with simpler substances which also show a tendency to polymerization. Actually, the changes induced by "ripening" can be reversed by means which, admittedly, lead to depolymerization. As, however, the use of heat is essential and fairly high temperatures, exceeding 300° C., are required, it is not surprising that the complicated raw materials are not simply dissociated with formation of their monomeric constituents, but that a whole series of secondary reactions occur simultaneously.<sup>2</sup> Yet by so-called "running" or "sweating" that is suitable, lengthy and intensive heat treatment, "run gums" can be obtained from the practically insoluble copals, and even from amber, which compare with regard to solubility with recent resins. It should, however, be added that these residues are devoid of all mechanical strength.

A peculiar position amongst natural resins must be reserved for sticklac and shellac. One peculiarity consists in the fact that this product is not a vegetable secretion, although this was formerly supposed, but is a product of animal metabolism. Sticklac is the product of the so-called lac insect, of the *Lakshadia* family,<sup>3</sup> which is a parasite on numerous vegetable hosts

See the Summary on Fossil Resins (*Farbe und Lack* (1927), 359, 378).

<sup>2</sup> More particularly, carbon dioxide is liberated from resinolic acids; see H. Wolff (*Farbe und Lack* (1924), 360, 405). Regarding the alteration in the numerical characteristics caused by heat treatment, see Lewkowitsch (*The Analyst*, 26, 37). Regarding the copal oil produced by running, see, *inter alia*, Wallach und Rheindorff (*Ann.*, 271, 308) (1892); Gill and Nisnida (*The Oil and Colour Trades Journal*, 1925, 193); see also Gildemeister (*Aether. Oele*, 1913, II, 9).

<sup>3</sup> According to Mahdihassan; see Abstract in *Farbe und Lack*, 1926, 630.

## INTRODUCTION

growing in India and the neighbouring countries.<sup>1</sup> Direct proof that the resin must be an animal secretion is afforded by the fact that the various kinds of shellac are practically

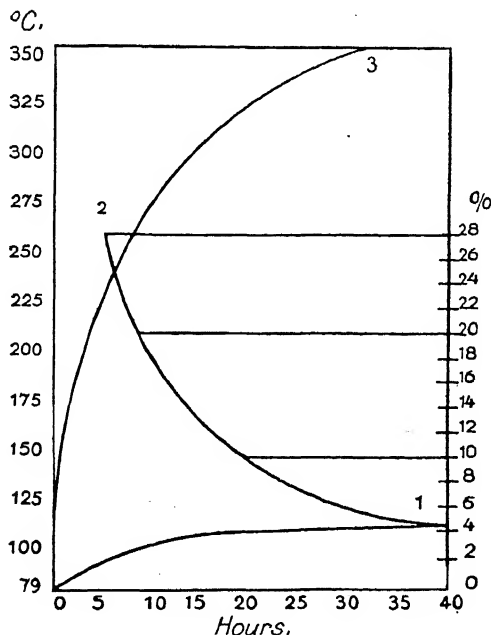


FIG. 1. TRANSFORMATION OF SHELLAC ON PROLONGED HEATING

(From H. Stäger, *Kolloidchemische Technologie*, p. 292)

Curve 1. Loss of weight of shellac at 100° C.

Curve 2. Loss of solubility of shellac in alcohol.

Curve 3. Rise of melting point of shellac.

identical chemically, in spite of slight other differences. Otherwise considerable differences would occur between the various kinds of shellac, which are produced on differing host plants, and these do not in fact exist.<sup>2</sup>

Shellac, moreover, behaves in a quite remarkable manner,

<sup>1</sup> The host plants belong to more than fifty families.

<sup>2</sup> Thus aleuritic acids prepared from various shellacs show the same characters; W. Nagel (*Ber.*, 60, 605, 1927); see also A. Endemann (*Angew.*, 20, 1776, (1907); 22, 676 (1909)).

by which it is distinguished from all other natural resins.<sup>1</sup> Whilst the ripening of ordinary vegetable resins cannot be imitated by heating alone, on simply heating shellac, for example, by prolonged heating at 100° C., its properties are greatly altered; its solubility in alcohol is rapidly reduced, whilst its melting point is greatly raised, until it becomes practically infusible. These relations are shown in Fig. 1, which represents graphically the results obtained by H. Stäger.<sup>2</sup>

Apart from a very slight loss of water the elementary composition of the resin remains unaltered, and the saponification value remains practically unchanged. The transformation caused by heating is irreversible. A similar change can be effected by the action of mineral acids, in which case the tendency to hydrolysis, but not the solubility in alkali, vanishes. In this case the solubility in alcohol can be restored by treatment with glacial acetic acid or formic acid and precipitation by water, although the capability of hydrolysis is only restored by redissolving in alcohol and again reprecipitating by water. Harries and Nagel, and also Evers,<sup>3</sup> who investigated these phenomena, came to the conclusion that they were due to aggregations and disaggregations, which caused changes in the degree of dispersion. Mutual absorption phenomena, due to surface tension effects, probably play a part in these changes. (Formation of association colloids; see page 54.)

**Technical Importance of Natural Resins.** This depends mainly on the production of suitable varnishes by solution in organic solvents. It is of importance that by suitable choice of solvents either so-called spirit varnishes, with alcohol, ethyl acetate, acetone, butyl acetate, etc., as solvents, or so-called volatile varnishes, with hydrocarbon solvents, can be produced. Apart from these two classes of "thin" varnishes, thick varnishes can also be prepared from the natural resins,

<sup>1</sup> A somewhat similar behaviour is shown, but only under the influence of an enzyme, by so-called Japan lac, the milk-sap of *Rhus vernicifera*.

<sup>2</sup> From *Kolloid-chemische Technologie* (Th. Steinkopff, Dresden and Leipzig, (1927), p. 293, Fig. 139).

<sup>3</sup> *Wiss. Veröff. Siemens-Konz.*, III, 248, 253 (1923); *Kolloidzeitschr.* 33, 181 (1923); *Ber.* 56, 1088 (1923); *Angew.*, (1924), 117; see also H. Wolf (*Chem. Umschau*, 1916, 2).

which contain considerable quantities of drying oils, more especially linseed oil and wood oil.<sup>1</sup>

As varnishes can only be prepared from products which are soluble in suitable solvents, it is necessary to deprive copals of the valuable mechanical properties which they have gained by the ripening process by previous running.<sup>2</sup> Apart from this undoubted disadvantage the losses on running are considerable, amounting on the average to about 20 per cent. Moreover, the practical operation of the process is exceptionally difficult as small batches only can be worked, and there is no definite indication of the end-point. As, however, the correct degree of running is essential for the satisfactory admixture of the copal with the fatty oil (for otherwise the varnish may become clouded, either immediately or after some time, a defect known as "bloom"), it is clear that in spite of their very valuable properties the copals have many disadvantages as varnish resins.

Resins have important applications apart from the varnish industry. For example, cheap, saponifiable resins play an important part in the production of paper, soap, and so forth. Large quantities of various resins are also used in the linoleum and pyrotechnic industries, and more particularly in the electrical industry. For many such applications shellac is still considered to be the most suitable natural resin. Apart from its special suitability for electrical purposes, it is also much used for polishes and for the production of gramophone discs. In addition it possesses the property, shared by no other natural resin, of peptization by weak alkalies, more particularly by dilute borax solutions, a property which is largely utilized for the production of textile dressings and for the manufacture of inks, washes, and so forth.

The exceptional mechanical properties which natural resins may acquire by ripening are only utilized on any extensive scale in the case of amber. In this product the valuable mechanical properties, which are associated with exceptional

<sup>1</sup> On the classification of the various varnishes, see Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), p. 284 *et seq.*

<sup>2</sup> On experiments on the direct solution of copals, see Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), p. 342.

adaptability to mechanical working, are much more highly developed than is the case with the hardest copals. Whilst, therefore, amber has been widely used for thousands of years for decorative purposes, and the continued manufacture of countless products for daily use ensures a market for the considerably increased production of this raw material,<sup>1</sup> it has not been found possible to introduce the use of copals for similar purposes.

The production of natural resins is very large. Thus the annual production of colophony (rosin) is estimated to be about 400,000 tons. The annual production of copals and other resins, apart from colophony and shellac, is probably about 30,000 tons, whilst that of shellac is probably equally large or even larger.<sup>2</sup>

Germany takes no part of any practical importance in the output of natural resins. Apart from amber, which is a German monopoly, only relatively unimportant quantities of colophony are produced, which are negligible in comparison with the home consumption. The imports of resins are therefore very considerable, as will be gathered from the table below, which has been compiled after deduction of the re-exports.<sup>3</sup>

NET RESIN IMPORTS INTO GERMANY, IN METRIC TONS,  
FOR THE YEARS 1913, 1925, AND 1926

VARIETY OF RESIN	1913	1925	1926
Colophony (Rosin) . . . . .	96 265.2	58 048.6	46 507.4
Copals . . . . .	5 357.3	4 397.4	3 163.7
Other Resins . . . . .	4 737.0	2 544.0	2 135.8
Shellac . . . . .	3 950.0	2 917.6	3 098.8
Total Value (Marks) . . . . .	41 685 000 (£2,084,250)	45 500 000 (£2,275,000)	39 125 000 (£1,956,250)

<sup>1</sup> The annual production in 1912 may be estimated at about 500 tons. For varnish production, rather more than 100 tons of "sweated" amber are annually available; the total amount of amber present in the "blue earth" has been carefully estimated by Goeppert, and is believed to amount to about 5 million tons. See W. Boelsche, *Bernsteinwald*, Stuttgart (1927), pp. 41, 43.

<sup>2</sup> The annual value of the shellac dealt with in India is about £5,000,000; see *Farbenztg*, 32, 2429 (1927).

<sup>3</sup> Based on the official Import and Export Statistics.

## INTRODUCTION

**Problems and Aims of the Artificial Resin Industry.** The artificial resin industry has to take into account the fact that natural resins are produced in sufficient quantities, of quite satisfactory quality and in part at very reasonable prices. One very definite problem of the industry is the production of artificial products as substitutes for certain natural resins, such as shellac and copal substitutes. But it would be an error not to recognize that the aims of the industry are considerably wider than this. Natural resins are certainly very valuable products, which possess the not unimportant advantage that the consumers are accustomed to their use, and the manufacture of artificial substitutes of at least equal quality at reasonable prices is in any case very difficult. It should, however, always be remembered that the natural resins possess disadvantages, which are not especially emphasized for the simple reason that they are for the present unavoidable. The production of artificial products offers the possibility of varying the properties widely, and more particularly of increasing certain desirable qualities to a degree which is absolutely impossible with natural products. In this way possibilities are open to the artificial resin industry, which may lead to wide demands for its products by the use of these as the basis of entirely new industries.

The truth of the above standpoint is obvious if one reviews the history of the artificial resin industry. The earliest artificial resins were the coumarone resins, which were invented in 1890, and which were tried as substitutes for colophony shortly after their discovery. This attempt inevitably failed as they offered no particular advantages for the purpose, and there was therefore no special inducement to use them. Conditions were more favourable in the case of the artificial shellacs which have been marketed since about 1902, consisting essentially of condensation products of formaldehyde and phenols. For although these products presented many serious disadvantages which appeared to render their use for many purposes inadvisable, they offered not merely advantages in price, but also numerous possibilities of application which enabled them advantageously to replace natural shellac in many cases.

The new artificial resin industry scored a real triumph in

1907 by the discovery of phenol-formaldehyde condensation products capable of being hardened, by L. H. Baekeland<sup>1</sup> and H. Lebach.<sup>2</sup> These materials could be prepared in the form of liquids or of solids which were readily soluble and of low melting point, known as "primary condensation products," which correspond in character to the ordinary recent natural resins.

These new products were characterized by a property hitherto quite unknown. It was at that time not yet realized that shellac was to some extent convertible into insoluble products of relatively high melting point; the new artificial products possessed this property to a very much greater degree, and could be converted in a few minutes, by suitable treatment, into secondary products which were very hard, did not soften on heating, were extremely resistant chemically, and insoluble in practically all solvents. These properties opened up possibilities which led to the establishment of entirely new industries. Simultaneously, the discovery of these products led to a rational manner of producing plastic masses resembling amber and other products, the industrial applications of which greatly exceeded those of amber, horn, and other naturally available materials.

It might be said that since that time the artificial resin industry has been unable to achieve another success of equal importance, but the further progress which has been made by the definite and systematic development of the earlier results is by no means small. Not only have earlier defects been completely overcome, but numerous new methods have been tried which cover almost the entire field of organic chemistry. It must be admitted that the application of artificial resins is still relatively small, the world's production being estimated at about 30,000 tons annually. The reason for this relatively limited development is, however, to be found less in defects of the products, many of which, such as the new copal substitutes, are fully equal to or even superior to the natural resins in quality, than in the difficulty arising out of the low prices of the natural products.

<sup>1</sup> *Chem. Ztg.*, 1909, 317, 326, 347, 353, 1268; 1912, 1245.

<sup>2</sup> *Angew.* (1909), 1598. *Chem. Ztg.* (1913), 733, 750.

It should particularly be noted that during the war and post-war periods the artificial products have proved invaluable in spite of their inherent defects, and to others due to lack of suitable raw materials for their manufacture. Even the relatively despised coumarone resins played an important part during the war, as without them almost the whole of the paint and printers' colour industry would have been paralysed. It was, of course, unavoidable that they should be used for purposes for which thin paints would be unsuitable under normal conditions, for example, for external use, and it is quite unfair to form an adverse opinion on the ground of the rapid depreciation of such paint, which was only to be expected in the circumstances.<sup>1</sup>

The question might be raised whether the artificial resin industry should not, methodically, endeavour to synthesize the natural resins. There can, obviously, be no question with regard to the scientific interest of such a programme, but from the technical standpoint there would be fairly general agreement that any such attempts should at least be confined to certain special natural resins, perhaps more particularly to shellac.<sup>2</sup> One reason for this view is that the natural products, although they possess undoubted good qualities, are far removed from being ideal for their purposes, and might therefore be superseded. Another reason is that the achievement of the production of materials possessing the properties of resins by methods entirely different from those made use of in nature, which latter are, moreover, still quite unknown, suggests that attention should be directed less to the production of definite structural complexes than to the achievement of a physical condition, which is dependent on other considerations.

This leads us to a question, the answer to which is not

<sup>1</sup> After internal application absolutely normal durability was achieved, but the production of light-coloured paints fast to light was found to entail difficulties which it was impossible to overcome.

<sup>2</sup> Regarding a method which is technically possible, see German Pat. 449,275 (Siemens-Halske, A.G.); see also J. Scheiber and W. Noack, British Pat. 252,715; U.S. Pat. 1,660,094; French Pat. 616,670; Swiss Pat. 123,163; C. (1928), I, 2,462.

Regarding the synthesis of constituents of guaiacum resin, see O. Doebner *Arch. Pharm.*, 234, 610, 1896).



without importance, namely, as to whether the causes for the production of a resin can be discovered or not. Such an inquiry embraces the question as to whether there are essential differences between natural and artificial resins, and more particularly whether any such differences may exist which affect their technical suitability. If one were to arrive at the conclusion that, apart from the question of origin, there was an essential analogy between the natural and artificial products, this would entail an essential freedom in the choice of methods for the production of the latter, which would be of the greatest importance. More particularly it would then be quite obvious that it would be irrational to attempt to synthesize the natural resins, an achievement which would presumably only be possible in a somewhat remote future.

## CHAPTER II

### THE TYPICAL PROPERTIES OF RESINS

ACCORDING to A. Tschirch,<sup>1</sup> the conception of a "resin" is purely empirical. Apart from vegetable origin, the decisive reasons for including a substance among the class of resins may be described as a "totality of properties," amongst which chemical characteristics are of minor importance and physical peculiarities predominant, as is shown by the following summary—

#### CHARACTERISTIC PROPERTIES OF RESINS

##### ACCORDING TO A. TSCHIRCH

1. Vegetable origin.
2. Insolubility in water.
3. Solubility in alcohol, or in ether, or in both.
4. Relative insolubility in petroleum ether.
5. Softening on heating.
6. Fusibility, with formation of a more or less clear, adhesive liquid.
7. Adhesive character of the solutions.
8. Property of the alcoholic solutions of drying to form a transparent varnish, i.e. capacity for forming films.
9. Relative resistance towards reagents.
10. Complete resistance to putrefaction.
11. In some cases formation of resin soaps on treatment with alkalies.
12. Burning with a sooty flame.
13. Complete resistance to rancidity, etc.

The first point to be noted is that the above table is inapplicable to certain undoubted natural resins, as the copals and amber, for example, do not show the above solubility relations, or at most to a very insufficient degree. On the other

<sup>1</sup> *Die Harze und die Harzbehälter*, Second Edition, Leipzig (1906), p. 3.

## ARTIFICIAL RESINS

hand, numerous artificial products comply with all the requirements, naturally with the exception of the vegetable origin. It therefore appears very questionable whether the origin of any substance should be considered as in any way decisive as to its classification amongst the resins, if the other conditions are fulfilled, even though the definitions of Tschirch were otherwise retained.

One might be tempted to include both natural and artificial resins under a new collective name, and to reserve the term "resin" for otherwise conformable vegetable secretions, but one may well decline to adopt this view, as age-long custom has established the use of the word "resin" in all the arts, and the distinction now usual between the "natural" and "artificial" products is quite sufficient. It would, however, be a mistake to consider the origin as in any way characteristic.

The external character of any material is the first criterion for its recognition as a resin. A vitreous-amorphous texture already suggests a resinous character, whilst a further recognition of the origin and character of the product is largely a matter of personal experience; in the case of natural resins such further recognition is not especially difficult. The vitreous-amorphous condition may, however, be replaced by a clouded amorphous or even a clouded crystalline appearance, without excluding the material from the category of resins. As a further criterion one must study the behaviour of the material on heating, and more particularly that of the cooled melt. If, for example, the latter shows no tendency to crystallize over a considerable time, there is no reason why it should not be considered to be a resin; certain varieties of colophony and benzoin resin are fairly frequently clouded crystalline in character.

This circumstance shows that the term "resin" characterizes a physical condition rather than any particular material composition, and the maintenance of a so-called amorphous condition is characteristic of the resinous state. It would, of course, be erroneous to consider the terms "amorphous" and "resinous" as synonymous, for resins are further characterized by the property of being capable of forming films.

Tschirch recognized the importance of this character by

requiring that the alcoholic solutions of resins should dry to form varnishes. In this form the criterion is certainly too limited, as on the one hand by no means all resinous products are soluble in alcohol, and on the other allowance must be made for the degree of ripening, or of condensation or polymerization in the case of artificial resins. With regard to solubility, it is certainly inessential whether the solvents alcohol and ether are effective, or whether the solubility in petroleum ether is small. The only decisive question is whether the material is soluble, and whether the solutions possess the characteristics of a thin varnish, that is, whether they form a film when a thin layer is evaporated. It is not even justifiable to demand that the solutions in every solvent shall have the character of a varnish. Thus, for example, a solution of sandarac resin in alcohol forms a clear and continuous film, whilst the solution in a mixture of 75 per cent of ether and 25 per cent of benzene leaves a dull residue. The solutions of many natural resins in carbon tetrachloride also form dull films. If in the case of the solution of sandarac resin in a mixture of ether and benzene the proportion of benzene is increased, or if other mixtures are used, the dull film may even lose all internal cohesion. Residues are then obtained which resemble those which are always obtained from amorphous, non-resinous materials, when deposited from solution. Similar conditions can easily be obtained with the artificial products.<sup>1</sup>

If one therefore recognizes the necessity of requiring, apart from solubility, the varnish-forming character in the case of solutions in *suitable* solvents only, one can but reasonably admit that the special condition of the product must be allowed for. It is clearly impossible to deny the resinous character of amber, because it does not conform to the too rigid conditions laid down by Tschirch, and more particularly because it is not directly able to form varnishes. The same considerations apply to certain artificial products which, in their "final" state, considerably exceed even amber, after its millions of years of ripening, in resistance to the action of solvents, whilst the corresponding "primary" resins readily form varnishes.

<sup>1</sup> See H. Wolff, *Farbenztg.*, 25, 668 (1919-20).

Every resin originates from raw materials which do not themselves show any resinous characters. The development of the processes leading to resinification depends on a number of factors which can obviously not be readily established in the case of the plant, whilst when preparing artificial products they can at least be approximately determined. Preliminary compounds are first formed, which ultimately produce the actual resin. The further transformation of the product is then merely a consequence of hitherto latent potentialities of reaction, the more or less complete course of which is dependent on special conditions. The sequence of reactions in the formation of both natural and artificial resins are tabulated below—

NATURAL RESINS	ARTIFICIAL RESINS
Unknown primary materials.	Known primary materials.
Unknown intermediate compounds.	Intermediate compounds, usually known.
Balsams, turpentine.	Liquid resinous products
Recent resins.	Soluble "primary products."
Recent fossil resins.	"Intermediate products" softened by heat, which gelatinize with solvents.
Fossil resins.	"Final" products.

These two reaction sequences, tabulated above, are completely analogous, but the periods within which the various processes are realized can be enormously shortened in the case of the artificial products. But just in the same way that a fossil resin originally possessed recent characters, so an artificial "end" product necessarily passes through the intermediate stage of a soluble resin. Therefore in deciding whether any particular product is, in fact, a resin, the decision must not rest solely on the actual condition of the sample, but regard must be paid to the preliminary stages through which it has passed before a decision can be made. If these preliminary stages correspond to the characters expected of a resin, then the product which has ripened or been artificially altered until it no longer remains in the soluble and fusible condition, is still a resin.

The above considerations show that when investigating the causes of the resinous condition, one may confine oneself to phenomena which characterize both recent natural resins and

soluble, "primary" artificial resins. Apart from the question of solubility, which has already been dealt with, all these products show the property of gradual softening when heated, followed by undecomposed melting to form a more or less clear and adhesive liquid. Tschirch emphasized both these peculiarities, which are characteristic of *mixtures* of substances, which possess the property of mutual solubility.

No characteristic chemical criteria are available, and no such criteria are cited by Tschirch. For the chemical inertness is, of course, merely a consequence of the neutral character of the substances present in the mixture. It must not be concluded from the occasional property of resins of forming resin soaps that constituents of similar characteristics, i.e. acids, esters, lactones, or anhydrides, are *necessarily* always present.

It is logical to reserve the term "resin" for mixtures of *organic* substances, a view endorsed by Tschirch by the requirement that the substance shall burn with a smoky flame, apart from his requirement, now abandoned by us, that it shall be of vegetable origin.

We may therefore, provisionally, accept the following characteristics of resins—

- (a) Organic composition.
- (b) The character of a mixture of mutually soluble constituents.
- (c) Solubility in suitable solvents.
- (d) Capability of forming films on evaporation of the volatile solvent used for solution.

In consideration of what we have already discussed we may, therefore, propose the following definition—

"Resins" are natural or artificial mixtures of organic substances, which at any rate originally possess the properties of solubility, of softening gradually, of fusibility, and also of separating from solutions in suitable solvents, on evaporation of the same, in the form of films.

This more or less descriptive definition of that which may be considered to be a resin calls for criticism, in so far as it would include various substances as resins which are not customarily included in that category.

Thus Tschirch already included in his characteristics insolubility in water. This must be considered as something more than the statement of a requirement which is frequently of technical importance,<sup>1</sup> as it also excludes the vegetable gums and mucilages, which are of carbohydrate character. From certain standpoints one may agree with this limitation, but it is impossible to ignore the fact that these carbohydrate products show essentially resinous characteristics in many respects; more particularly, they also form films, and they cannot readily be distinguished from resins, even by an experienced specialist. The fact that some of these products cannot be melted without decomposition is not decisive, because insolubility and infusibility do not necessarily go together, and a material may be both soluble and infusible. Thus in a certain sense artificial products of carbohydrate character, such as the dextrines, may possess resinoid characters, which are entirely in accordance with their film-forming character. Moreover, such substances are association-colloids (see page 54) which include many members of resinous character.

Asphalts, pitches, and bitumens, of both natural and artificial origin, must certainly be included amongst the resins. Even the natural members of this group must be considered to be in a sense artificial, for they have not been produced by any process comparable with the secretion of ordinary resin, but by a series of destructive and synthetic reactions which, in spite of the absence of human interference, are of essentially the same character as artificially regulated processes.

Fatty drying oils are not themselves resins, but serve as raw materials for their production, as the oxynes which are formed from them by a complicated series of reactions are of undoubted resinoid character.<sup>2</sup> Moreover, the reactions leading to the formation of such oxynes presuppose polymerization, of which the reactive constituents of the fatty acids are capable in virtue of their unsaturated complexes, either directly or after oxidational

<sup>1</sup> The solubility of a resinous product in water may on occasion be very desirable, particularly if the film which remains after evaporation of the water may become insoluble in that liquid, as in the case of certain new products, the "Schellan" products.

<sup>2</sup> See A. Eibner, *Angew.*, 36, 34 (1923).

change.<sup>1</sup> Moreover, there exists a far-reaching analogy between substances capable of polymerization, which by that means produce resinous products, and the fatty drying oils.<sup>2</sup>

It is more difficult to decide whether the cellulose esters should be classified as resins. These products undoubtedly comply with all the requirements of the definition given above. There, therefore, appears to be no justifiable reason for excluding them from the category of resins. The circumstance that they are united as a definite group of chemical individuals cannot be considered as an argument to the contrary, for, as will be shown later, it is necessary to regard the resins as matter in a special state, which happens to occur regularly under certain conditions which are always present in the case of the cellulose esters, and this circumstance in no way entitles one arbitrarily to exclude this class of substances on the grounds of their chemical constitution.

In general, the above definition obviously leaves room for individual personal opinion. As soon as the old definition of a resin is dropped, with its dogmatic insistence on the requirement of vegetable origin, which makes the collective classification of these very varying vegetable secretions relatively easy, and when the attempt is made to apply an old term in a modern sense, one is naturally more or less exposed to difficulties of delimiting the definition in its new sense. Such difficulties would occur in any attempt to co-ordinate a group of substances on consistent principles under any collective name, whether new or old. It seems very doubtful whether the adherents to the old, and certainly obsolete, definition of a resin would gladly acquiesce in any other collective descriptive term, of which many are possible.

Having now endeavoured to define in general terms the properties which characterize resins, we may attempt to investigate the real causes which underlie these peculiarities.

<sup>1</sup> See J. Scheiber, *Angew., Farbe und Lack* (1926), 295; (1927) 75; *Chem. Umschau*, 34, Part I (1927); *Angew.*, 40, 1279 (1927); see also A. Eibner, *Farbe und Lack* (1926), 378, 403.

<sup>2</sup> This is particularly clear from the behaviour of olive oil, which is ordinarily considered as the type of a non-drying oil. If this product is exposed to the rays from an ultraviolet quartz lamp, normal drying occurs. (See A. Eibner and H. Rasquin, *Chem. Umschau*, (1926), 36.) This behaviour is very similar to the phenomena characteristic of photopolymerization.



## CHAPTER III

### GENERAL CAUSES OF THE EXISTENCE OF RESINS

If a solution of a solid substance is evaporated, the following may occur—

(a) That portion of the dissolved substance which is in excess of the limit of solubility may separate in the form of *crystals*.

(b) The solid may separate in the form of an amorphous deposit.

(c) No visible separation of material occurs, but the solution steadily becomes more viscous as the concentration increases, and the solid matter finally remains in the form of a vitreous mass.

The phenomenon described under (c) is characteristic of resins, but it should be noted that the alternatives described above by no means necessarily occur exclusively, and that, on the contrary, any possible intermediate conditions may occur.

Regarding the causes for the occurrence of one or other of the above alternatives, certain conceptions have been developed by F. Haber<sup>1</sup> and by P. P. von Weimarn.<sup>2</sup>

According to Haber, whenever the saturation limit is exceeded, that is, whenever deposition occurs through accumulation of solid or concentration of a solution, the character of the deposited solid material, amorphous or crystalline, is decided by the relation between the so-called Velocity of Agglomeration (H) and the so-called Velocity of Orientation (O). The agglomeration velocity depends on the degree to which the local concentration of the molecules in question exceeds the solubility limit, and on the degree of mobility of the molecules in the liquid from which they separate. In

<sup>1</sup> *Ber.*, 55, 1717 (1922).

<sup>2</sup> See more especially the summary by P. P. von Weimarn and T. Hagiwara, *Kolloidchem. Beihefte*, 23, 400 (1927).

consequence of the increasing zone of molecular attraction, due to the kinetic energy of the heat, linkages occur of a loose and irregular character, forming agglomerations which, when of sufficient size, are visible as flocks (amorphous flocks). The greater the agglomeration velocity, the more irregular will be the association into heaps which is essentially ruled by chance. Thus there arises a tendency to the establishment of equilibrium, which is accompanied by a loss of free energy. The Orientation Velocity is the velocity of conversion of the flocks into space-lattice orientations.

Thus  $H > O$  indicates predominance of the amorphous state; and  $H < O$  indicates predominance of the crystalline state.

The possibility (c) at the beginning of this chapter is, undoubtedly, associated with predominance of the amorphous state, as the occurrence of vitreous structures is essentially a peculiar form of amorphism, so that the conditions just described as characteristic for the development of ordinary amorphism must apply in this case also. We must therefore determine the differences between ordinary and resinoid amorphism.

We have already pointed out (Chapter II) that the property of forming films, which is characteristic for resins, is largely dependent on the choice of a *suitable* solvent when preparing the necessary "varnish." Although some resins are not particularly sensitive in this respect, it is a general practical experience that among the available solvents a selection must be made with great care in order to obtain a film of the best possible quality. Therefore a film is certainly a structure in the formation of which the solvent plays a dominant part.

This fact can only be explained by assuming that a mutual effect is exerted between solid and solvent, upon the influence of which the character of the film depends. In the nature of things this can only take the form of solvation (solvate formation).

The act of solution of any substance is actually a solvation process, as has been emphasized more particularly by von Weimarn.<sup>1</sup> This applies not only to true solution, but also to the formation of dispersions which must be considered

<sup>1</sup> *Kolloid-Ztschr.*, 2, 203 (1908).

colloidal. In the case of resins, which are always mixtures, the character of the solutions will be especially complicated, as the individual constituents will be dispersed with varying degrees of facility and to varying extents. In any case, regular solution can only be assumed in relatively few cases. There is the additional complication that at the commencement of the saturation processes leading to the formation of a film, association may lead to the formation of colloidal phases with increased concentration, and this applies even to systems which are originally molecularly dispersed.

The more definite the lyophilic character of the individual constituents of the resin, the more favourable will be the conditions to the formation of a gel-structure, that is, of a film. Any circumstances which cause lyophobic characters must impair the possibilities of film-formation to a greater or smaller extent. These considerations furnish the key to an explanation of the wide variations in film-forming capacity of one and the same resin. Moreover, they partially explain the difference between ordinary and resinoid amorphism.

We must also take into account another factor which plays an important part in the behaviour of resins, namely, their character as mixtures. In order to produce a resin it is in no way sufficient merely to mix any unselected materials at random, as the constituents of the mixture must, so to say, be mutually suitable. If this condition is fulfilled, each of the ingredients taken singly, that is, in the pure state, may be capable of crystallization, and need by no means be amorphous in the ordinary sense. In fact, the investigations of natural resins so far carried out have led to the discovery of the presence of very considerable quantities of well crystallizable constituents, and the circumstances are quite analogous in the case of artificial resins.

Although for the time being it is difficult to explain in detail the conditions which mixtures must fulfil in order to constitute resins, it may be said that the power of mutual solubility is certainly one of the main factors. Regarding the necessary chemical conditions, no conclusions can be drawn at present from the investigations of natural resins. But from certain

possibilities of production of artificial resins, which certainly owe their film-forming properties but very little, if at all, to colloidal phenomena, one may draw the conclusion that the conditions are especially fulfilled by mixtures of substances of the same chemical character.

This conclusion is of importance, as according to the view of various investigators<sup>1</sup> the conditions for the formation of solvates are particularly favourable when the solute and the solvent possess groups in common. In the case of substances of the same chemical character, for example, mixtures of isomers and homologues, this condition is obviously fulfilled. It may, therefore, be assumed that in such admixtures the part otherwise played by the volatile solvent may be fulfilled by one or other of the solid constituents of the resin mixture. A dry film produced in this manner owes its character to the presence of a solid solution, or to that of a super-cooled melt, which is much the same thing.

Resinoid amorphism is thus characterized by the fact that it usually occurs in lyophilic mixtures, the individual constituents of which possess a more or less marked degree of mutual solubility.

In order to deal with a possible objection, we will here draw attention to the following: Even in the case of a resin containing constituents which undoubtedly possess mutual solubility, naturally no film formation can occur if the homogeneity of the system has been largely destroyed by previous desolvation, or by precipitation of certain constituents. This case occurs, for example, if a relatively non-volatile non-solvent is added to a readily volatile solvent, by the evaporation of which alone normal film-formation occurs. If such a solution initially shows normal, that is, clear, character, the degree of dispersion may already have been affected. But the degree of dispersion is more particularly affected as the more volatile component of the solvent evaporates, as a steadily increasing proportion of the non-solvent is then present. As soon as this leads to the separation of important constituents of the resin the film-formation must necessarily be impaired. This process may be

<sup>1</sup> E.g. Fredenhagen, *Zts. phys. Chem.*, 98, 66 (1921).

carried so far that, in the solidifying system, ordinary amorphism ultimately replaces resinoid amorphism. If a rough, dull film, produced in this way, is then melted, that is, if the separated resin constituents are allowed to exercise their mutual solubility, a normal film is formed on cooling. The same effect is produced by the action of the vapour of a suitable solvent.

Thus according to Haber's views, resins must be considered to be a sub-class of amorphous substances, namely, those in which the agglomeration velocity attains and maintains an effective predominance over the orientation velocity. We must now investigate what causes may maintain the former large and the latter small.

Haber bases his views on those of Tammann,<sup>1</sup> who deals with the question of supercooled melts. According to Tammann, a supercooled melt of a single chemical individual represents an immense, random heap of molecules, the further history of which depends on the orientation velocity. The orientation process itself, that is, the crystallization, may be divided into two stages, germ formation and germ growth. According to the experimental evidence germ formation in the supercooled melt is very remarkably retarded, particularly at temperatures much below the melting point, in the case of molecules containing a large number of atoms, as is often the case with organic compounds. But even after germs have been formed, they may or may not be able to grow. In general, the low temperature at which germ formation occurs is not favourable to further growth.

This behaviour is explained by Haber as follows<sup>2</sup>---

The individual molecules in the random molecular heaps are not fixed. The forces with which they interact tend to re-arrange them into a space-lattice form in which the potential energy is at a minimum. In the crowded aggregate within which the molecules are located the development of these molecular forces is the more retarded the more the molecules are interlocked. The motion due to heat facilitates the orientation process by means of molecular impacts of suitable direction and strength, as long as it does not become excessive. . . . The stability of the first orientated molecular aggregates, which comprise a few

<sup>1</sup> *Kristallisieren und Schmelzen*, Leipzig (1903); *Aggregatzustände*, Leipzig (1922).

<sup>2</sup> *Loc. cit.*, pp. 1720-1721.

molecules only, requires a temperature which is appreciably and even very greatly below the melting point, as these early aggregates represent a very much weaker association than do the larger crystals. This can be easily realized from the consideration that the process of crystal growth is due to attractional and repulsive forces, of which the attractional forces diminish more slowly with increasing distance than do the repulsive forces. Consequently the repulsive forces affect the neighbouring molecules only, whereas the attractional forces are active over a wider distance and therefore cause a rigidity of association of the molecules of larger crystals which is lacking in the smaller orientated groupings.

Experiments by von Pickardt<sup>1</sup> have shown that the crystallization velocity of a substance which normally crystallizes easily and rapidly, namely, benzophenone, is very considerably decreased by the addition of very minute amounts of soluble materials. By taking this fact into consideration together with the views enunciated by Tammann and by Haber, the cause of the resinoid state can very well be explained on the supposition that the mixtures in question possess to a greater or less extent the character of supercooled melts, in which the, at least partial, mutual solubility of the constituents still further reduces the crystallization velocity, which is in any case small, on account of the large and complicated molecular structure of the constituents.

P. P. von Weimarn<sup>2</sup> has published a number of objections to the views developed by Haber, which must be considered more closely, as he develops a standpoint which appears to explain the phenomena with which we are concerned more clearly than is possible on the basis of the agglomeration and orientation processes.

Von Weimarn points out more particularly that it is quite inconceivable why the random heaps of molecules should at first maintain an "extremely arbitrary" form, instead of immediately forming spheres, which would correspond to the tendency to attain a minimum of free energy, that is, why crystals of the same size as the actual flocks should not form immediately, as otherwise the forces which cause the formation of the molecular clusters would appear to differ from those causing crystalline orientation, which is scarcely probable.

<sup>1</sup> *Ztschr. f. phys. Chem.*, 42, 17 (1902).

<sup>2</sup> *Kolloidchem. Beihefte*, 23, 400 (1927).

As a result of work extending over many years,<sup>1</sup> von Weimarn has developed the view that there is no such thing as a truly amorphous solid state, but only ultracrystalline, microcrystalline and macrocrystalline structures. The only criterion of "amorphism," in the sense hitherto used, is the size of the grain or particle. If this is below the limit of microscopic resolution the structure is "amorphous," whilst otherwise it is crystalline.

The following observations show that the degree of dispersion of the structural elements of crystalline structures exercises a very considerable influence on the general orientation—

1. Solutions of readily soluble substances, possessing no complicated chemical composition, and which separate in the same crystalline form throughout a wide temperature range when slowly crystallized, can only be obtained in the form of transparent jellies or glasses if very small volumes are used and are cooled with extreme rapidity.

2. Viscous solutions of extremely soluble substances of simple chemical composition, which can be obtained in exceptionally well-developed crystals by slow crystallization, but which occur in several modifications or form several compounds with the solvent, solidify to form transparent jellies or glasses on rapid cooling.

3. Jellies are most easily obtainable from solutions which contain several substances which are easily soluble in the solvent which is used.

4. As the molecular weight of the dissolved substance increases, the tendency to form jellies and glasses also increases.

Von Weimarn has also pointed out that if molten substances are cooled sufficiently rapidly, or if crystalline materials are sufficiently disintegrated mechanically, systems are obtained, the orientation of which is so slight that in spite of their solid state they can no longer be practically distinguished from liquids. Therefore a supercooled melt is considered to be identical with a mechanically produced ultramicrocrystalline system.

<sup>1</sup> The following is based on von Weimarn's summary (*loc. cit.*), in which all his previous publications are cited.

The nucleus of von Weimarn's views is the theory of vectoriality, which is to be considered as a development of M. L. Frankenheim's hypothesis on the crystalline character of all solid bodies.<sup>1</sup>

The characteristic of a crystal is its construction from molecules in accordance with definite symmetrical relationships, the thirty-two crystalline systems. The molecules themselves are also systems in space, the units of which are the individual atoms. The atoms within the molecule manifest a definite mutual orientation, which is, in principle, identical with that of the molecules in the crystal. In order to express this identity, von Weimarn defines both molecules and crystals as "vectorial" systems, that is, as systems which are orientated according to definite laws. In order, however, to distinguish molecules and crystals, the previous conception of the latter structures must be extended, as otherwise any vectorially constructed system might be considered to be identical with a crystalline structure. The theory of the vectoriality of matter serves this purpose.

The difference between molecule and crystal, both of which are vectorial structures, is immediately clear if one compares a giant molecule of a chemically, extremely complicated substance with a small ultramicrocrystal of the same size, for example, of gold. We can consider the problem from two standpoints, namely, from the ordinary chemical standpoint or from that of colloidal chemistry.

From the former standpoint the ultramicrocrystal consists of relatively numerous individual crystals, and can, therefore, be subdivided mechanically without destroying the chemical structure or interfering with the vectorial arrangement of its structural elements. In the case of the giant molecule, on the contrary, this is naturally impossible without decomposition. The difference may be expressed by saying that the crystal consists of a "vectorial polymerization," whilst the crystal represents a "finite vectorial structure."

From the colloid-chemical standpoint, it is immediately

<sup>1</sup> This theory was published in 1839 and has been maintained in spite of many attacks; see *Ann. d. Phys. u. Chemie.*, 72, 222 (1847).



evident that the true solution of the substance consisting of the giant molecules, and the dispersoid solution or dispersion of the ultramicrocrystals, must both result in systems very similar in their properties.

The conception of crystallization as vectorial polymerization of theoretically limitless extent leads to the conclusion that a solid substance can *only* appear as a crystal if nothing prevents the fundamental polymerization process. In order, however, that the tendency to crystallization, which is always present, may be exercised, the reactivity of the atoms fixed at the surface of the molecule must be able to act unhampered. This is not the case if the atoms in question are otherwise engaged in consequence of solvation, and so forth. The larger the size of a molecule, the smaller is the free reactivity of the surface atoms in consequence of the tendency to attach foreign molecules, that is, molecules of the solvent or of impurities. As, however, desolvation and autopurification are essential requirements for further vectorial polymerization, it is not surprising that with increasing molecular magnitude the degree of polymerization required for crystallization is more difficult to attain.

It is clear that, according to the views of von Weimarn, those mixtures, which experience shows to be characteristic of resins, are definitely predestined to be characterized by the non-development of crystals. Firstly, the conditions 3 and 4 of page 26 are present. Secondly, there is usually a pronounced lyophilic character. Thirdly, it must be borne in mind that impurities of a particularly active character are probably always present, and that this fact, together with the fact that the molecular dimensions are usually considerable, must render autopurification difficult.

This is not the place in which to pronounce a verdict on the views of Haber or von Weimarn, or to oppose the one theory to the other. Broadly speaking, either view gives a quite satisfactory explanation of the fact that certain material mixtures form resins. It seems comparatively unimportant that one or another typical property of resins is, perhaps, more plausibly explainable by one theory than by the other. It is,

however, important that both theories recognize the conception "resin" to denote a physical condition, which must inevitably occur under certain conditions. In this way the very basis for any discussion as to whether the term "resin" should be reserved for substances of any particular origin is annihilated. For regardless as to whether the term resin is reserved for vegetable secretions, and some other term, such as "solid jelly" or "organic glass," is chosen for the condition characteristic of such secretions, or whether, as is far more desirable, the meaning of the term "resin" is extended, it will always be necessary to consider the physical state of the natural secretions and the artificial products from the same standpoint.

It is now, however, possible to give definitions of the hitherto somewhat vague conception of a resin, which are in full agreement with the peculiarities of the substances concerned. From the standpoint of Haber's views on amorphism one may define the term as follows—

"Resins" are mixtures of organic substances, having the character of supercooled melts, which maintain their more or less definite vitreous character for the reason that their exceptionally low orientation velocity is unable to be exercised.

According to von Weimarn's views the definition would be as follows—

"Resins" are ultramicrocrystalline organic substances or mixtures, the capacity of which for vectorial polymerization (or regular crystallization) is so weak, in consequence of deficient tendency to adequate desolvation and autopurification, that the more or less pronounced character of a "glass" may be considered as practically stabilized.

Of course, these definitions make no claim to be in any sense final. Moreover, they refer quite generally to resins, whereas the earlier definition on page 17, which is based on other standpoints, may be considered to be more or less empirical.

165

## CHAPTER IV

### SPECIAL CAUSES FOR THE RESINOUS CHARACTER OF DEFINITE MIXTURES

THE natural and artificial resins represent numerous mixtures of substances, which may serve to test the views which we have already discussed. This control by means of practical examples seems desirable, in order to discover whether all the effective factors have been considered. A special investigation of this character is also desirable, as it is the only available method of securely establishing a theoretical basis for the production of resins by artificial means.

**Natural Resins.** In the case of the natural resinous products, which are essentially available in the finished condition only, an investigation of the causes of their resinous or vitreous condition can only be based on analytical results. In spite of the very great imperfection of our knowledge in many respects, it may be stated that the results of such investigations show, as a general rule, that these materials always consist of mixtures, which are usually very complicated; the isolation of the individual constituents often fails on account of insuperable difficulties.

This condition of admixture is, without doubt, a factor which is extremely favourable to the formation of resin, although it is in itself not necessarily sufficient. In actual fact, certain natural resinous secretions show definite crystallization phenomena, for example, certain "low-grade turpentine," from which resin acids crystallize, benzoin resin, elemi resin, some varieties of colophony, and so forth. On the other hand, the persistence of the vitreous condition in many cases is absolutely amazing; more particularly, the recent fossil copals and the fossil amber have persisted as typical "glasses" throughout thousands and even millions of years.<sup>1</sup>

<sup>1</sup> Compare the X-ray investigations of resins by S. von Naray-Szabó, *Biochem. Ztschr.*, 185, 36 (1927).

In the secretions of the so-called "resinolic" acid resins, according to Tschirch's classification,<sup>1</sup> the terpene products which are always present (the "ethereal oil"), without doubt, play an essential part in preserving the resinous condition. The resin acids which form the main part of the constituents are themselves substances which crystallize with comparative ease. If, therefore, the ethereal oil is removed, as occurs artificially in the industrial separation of the crude secretion, the turpentine, of the residue of colophony or rosin, and ethereal oil (oil of turpentine), the tendency to crystallization of the rosin, the residue of which consists mainly of resin acids, sometimes gains the upper hand. Under natural conditions, this only occurs if the main portion of the volatile terpenes is prevented from escaping. The turpentines obtained as products of the "secondary resin flow" must be considered to be solutions. On account of the very considerable proportion of ethereal oil, the concentration of these may very well be such that there is an exceptionally high orientation velocity (Haber), or very marked tendency to vectorial polymerization (von Weimarn) of the individual constituents, which overcomes the opposing tendencies, such as solvation and autopurification, so that visible crystals make their appearance. As soon, however, as the concentration of the solid, non-volatile products exceeds a certain limit, no further increase in size of any ultramicrocrystalline structures takes place, as autopurification, in particular, becomes permanently less active.

The terpene constituents have an undoubtedly strong tendency to form solvates with the resin acids, which are similar in chemical character, and the presence of these solvates increases the heterogeneity of the system considerably, by which means, from von Weimarn's standpoint, the maintenance of the vitreous state is facilitated. The very considerable effect of solvate formation is evident from the fact that so-called crystallized rosin, and also gum benzoin and elemi resin, when dissolved in a suitable solvent form varnishes which produce perfectly normal films.

<sup>1</sup> *Harze und Harzbehälter*, Second Edition, 1906, p. 28; the first communication is dated 1900.

Even ordinary solvents manifest a very considerable tendency, due to solvate formation, to be obstinately retained in resin films, at least in small quantity. In the case of the mixture of the terpene constituents of the ethereal oil with resinolic acids, the volatility is further diminished by autoxidation, whilst in the case of natural resin flow there is, in addition, the considerably diminished surface to take into consideration. This is the explanation of the fact that not only all copals, but even amber, still contain certain quantities of the original terpene mixture in more or less modified form.<sup>1</sup> This circumstance promotes the stabilization of such products in the form of a glass to a very considerable extent.

The resin acids are products, the peculiarities of which are manifested unmistakably in the direction of a complication of the original uniform character of the constituent materials. With regard to the conifer resin acids,  $C_{20}H_{30}O_2$ , it has been found that a whole series of isomers may occur, which show a very varying resistance to atmospheric action.<sup>2</sup> In particular, the sapinic acids, which may be regarded as natural products, are very unstable and manifest a considerable tendency to autoxidation, with formation of more or less complicated mixtures of substances which are in part closely interallied. It is not surprising that in this manner the commencement of visible crystallization is very considerably retarded, and that, as confirmed by actual observation of recent fossil and fossil products, this action, combined with the effect of the presence of the ethereal oil, maintains the resinous condition permanently.

Other factors, undoubtedly, play a part. Thus resinolic acid resins contain, more particularly, so-called resenes, which it is in many cases almost impossible to separate from the resin acids, although the resenes are neutral substances. As unsuccessful attempts to purify resin acids have shown, these resenes<sup>3</sup> are substances which are exceptionally easily peptonized, and

<sup>1</sup> See A. Tschirch, *Harze und Harzbehälter*, Second Edition, 1906, p. 742.

<sup>2</sup> See O. Aschan, *Chem. Ztg.*, (1924), 149-150.

<sup>3</sup> See, for example, the communications of P. Horrmann and N. Kroll on the purification of Manilla copal acid, *Arch. Pharm.*, 265, 214 (1927); see also J. Scheiber, *Ann.*, 453, 52 (1927).

may, for example, pass smoothly into solution in alkalis, together with the resin acids. Relations must, therefore, certainly exist between resenes and resin acids which oppose autopurification of the two classes of substances, and the growth of any ultramicrocrystals which might have formed; this amounts in practice to a direct influence in favour of the resinous condition.

The phenomena which take place during the so-called ripening process also, no doubt, exercise a considerable influence. This certainly includes a number of reactions, the chief of which are autoxidation and polymerization processes. We have already stated all that is necessary with regard to the former. With regard to the latter group of reactions, which endow the resin to a greater or less extent with the properties of a typical colloid, their stabilizing effect on the resinoid condition must certainly consist in especially marked solvation with the ethereal oil, and in increased complexity of the mixture as a whole and increased size of the molecules. Bearing in mind the fact that amber has been unable, in the course of millions of years, to exercise the tendencies to regular crystallization which are undoubtedly present, the sum total of the retarding influences must, in fact, be very considerable.

It is clear, that although our conceptions of the conditions are, without doubt, incomplete, the special causes for the resinoid condition of the resinolic acid resins and of the maintenance of this condition throughout geological periods are now recognized in principle.

For the other groups of Tschirch's classification of natural resins, the attempts to explain the occurrence of the resinoid condition rest fundamentally on the same basis. In the case of some of the substances in question, ethereal oils play but a small part or none. But in every case one or the other factor is present in addition to the complexity of the mixture, which is always recognizable, and together these ensure the continuance of the resinoid condition, at least throughout definite periods. In the case of benzoin resin, which is characterized by a relatively strong tendency for the development of plainly visible crystals, the factor, other than material complexity,

which maintains the resinoid condition, is the tendency to autoxidation of its main constituent, lubanol-(coniferyl)-benzoate;<sup>1</sup> in the case of the other products, classified as "resinotannol resins," it is the tendency to autoxidation of other complicated, unsaturated groups of compounds.<sup>2</sup> In the case of shellac, which occupies a special position as a product of animal metabolism, the wax which is present plays a certain part, in addition to the heterogeneity of the resinoid constituents, which must be considered as a mixture of various lactides.<sup>3</sup>

The effect of the various stabilizing factors will, of course, vary from case to case, as it is in every case dependent on the composition of the particular mixture. It is, therefore, not surprising that products occur among the natural resins, the resinous character of which varies considerably and is, in some cases, by no means very definite. One may draw the conclusion that there are undoubted relationships between the resinoid character and the chemical constitution of the components of the mixture, but the mistake must not be made of accepting the presence of any so-called "typical" groups as evidence of the resinoid condition. It is much more important that certain physical peculiarities, which must in turn be considered as a function of the chemical composition of each molecule, should exist to a marked extent. One may, in a sense, consider the relationships between resinoid character and chemical properties of the main constituents as indirect, whilst the relations between that condition and the physical properties are direct.

It is impossible to complete a discussion on the special causes of the resinoid state of natural resins without referring to Japan lac and to india-rubber products, as in these cases conditions are found which are in one sense different, but which, on the

<sup>1</sup> F. Reinitzer, *Arch. Pharm.*, 264, 133 (1926).

<sup>2</sup> These are mostly unsaturated "resin alcohols" or resinols. According to A. Tschirch, *Schweiz. Apoth. Ztg.*, 53, 61, 77; *C.* (1919), II, 673, the products of this class must be regarded as "protoretines."

<sup>3</sup> See, for example, C. Harries and W. Nagel, *Wiss. Veröff. Siemens-Konz.*, III, 2, 12 (1924); *C.* (1924), II, 1187. In actual fact X-ray investigation reveals the presence of definite crystalline nuclei in shellac resin; see S. von Naray-Szabó, *Biochem. Ztschr.*, 185, 87 (1927).

other hand, may be regarded as a link with certain artificial products.

On principle one could very well maintain that these products are not resins, and it is certainly surprising that Japan lac has always been regarded as a resin, whilst lactiferous secretions were only included in the system of resins by Tschirch on account of their contents of substances, such as albanes and fluavilene, of definite resinous character.<sup>1</sup>

Japan lac is a lactiferous secretion from *Rhus vernicifera*, which hardens with formation of an insoluble and infusible product as a consequence of oxidation and polymerization induced by enzymatic action. It is, therefore, essentially a product to be compared with the fatty drying oils rather than with ordinary resins. Of course, Japan lac is not a glyceride; its main constituent is Urushiol (Urushic acid), which is a mixture of pyrocatechins, substituted in the side chain by groups of varying degrees of unsaturation and of the formula  $(OH)_2C_6H_3.C_{15}H_{27}$ , which formula includes the varying degrees of unsaturation.<sup>2</sup> Without doubt, a parallel can be maintained between the sum of the processes resulting in the hardening of Japan lac, and the sum of those leading to the drying of fatty drying oils. In both cases the normal link between non-resinous preliminary products and insoluble end-products, namely, the ordinary soluble and fusible resin, is missing. The question, therefore, arises whether Japan lac should be regarded as a resin, or whether in future substances of this character, which form "resin" in a similar manner, should not be classified as "resin-like," which would undoubtedly be more rational.

In the former case the oxynes obtained from fatty drying oils would have to be classified as resins, as has already been proposed by A. Eibner.<sup>3</sup> In that case caoutchouc products would also be called resins, although, in the case of these products of the polymerization of unsaturated hydrocarbons,

<sup>1</sup> *Harze und Harzbehälter*, Second Edition (1906), p. 890.

<sup>2</sup> Regarding its constitution, see Majima, *Ber.*, 40, 4392 (1907); 42, 1419, 3864 (1909); 45, 2727 (1912); 46, 4080 (1913); 48, 1593, 1606 (1915); 53, 1907 (1920); 55, 172, 191 (1922).

<sup>3</sup> *Angew.*, 36, 34 (1923).



the true resinous intermediate product, characterized by solubility and other typical properties, is also often missing.

But consequences which are, perhaps, more serious than these considerations would arise regarding the classification of certain artificial products, as there is no distinction in principle between the natural polymerization of the caoutchouc-forming hydrocarbons which are present in the polymerized condition in the latex, and an artificial polymerization.<sup>1</sup>

The resin-like character of all these products is, of course, quite comprehensible in consequence of the typically colloidal character of their constituents, which are moreover highly complex, and the only question which might, perhaps, be raised is whether one should assume the presence of exceptionally viscous liquids, or of ultramicrocrystalline structures, or of both.

**Artificial Resins.** The artificial resins, which are in number and in variety of structure by no means inferior to the natural products, may be classified according to their general methods of manufacture.<sup>2</sup> From this standpoint we may distinguish :

- (a) Polymerization resins; and
- (b) Condensation resins;

being those which are primarily produced by polymerization or condensation respectively. It should be added that classification on this basis cannot be sharply defined, as in many cases the two operations are carried out conjointly. Thus, for example, many initial products must be described as condensation products, whilst the corresponding end-products are formed by polymerization. Apart from true polymerization, which is characterized by structural chemical changes, association and aggregation phenomena occur, which affect the physical properties of the product only.

<sup>1</sup> The circumstance that it is difficult to impart to the artificial products similar colloidal properties to those possessed by natural rubber is, of course, immaterial to the above considerations.

<sup>2</sup> A. Gerard, *Bull. Inst. Pin.* (1927), 191; *C.* (1927), II, 2013, distinguishes reaction resins, polymerization resins, and complex resins; A. Breguet, *Rev. Gen. Colloides*, 5, 681 (1927); *C.* (1928), I, 1235, defines the various forms of phenol-formaldehyde resins as molecular complex, isocolloid, and solid colloid solutions.

The causes for the resinous character of the artificial products are identical with those which determine that of the natural resinous secretions. No novel factors are observed.

In this case also, the main factor is the presence of a material mixture. The more complicated this mixture, the more well defined are the resinoid characteristics. Reactions which proceed simply and uniformly never lead to resin formation. This is more particularly evident from the results of reactions in which the conduct of the operation is decisive. As is well known, many substances which crystallize well and with comparative ease, and which can be obtained in good yields and even quantitatively, or at least as the main reaction product, can only be obtained in satisfactory quantity and of a satisfactory degree of purity if special regard is paid to their sensitiveness. As the conditions of reaction depart from a "mild" character, there is increasing difficulty in avoiding resinification, that is, the formation of "tarry products." In the preparation of artificial resins, one naturally proceeds in such a manner as to ensure that the primary action shall be accompanied by secondary reactions of all kinds to the greatest possible extent. It is in such cases of no importance, or only of conditional importance, to obtain any particular constitutionally defined individual substance, the required product being "resin." The considerable degree to which even many chemically pure substances are susceptible to subsequent change is quite surprising. Thus, for example, according to F. Raschig,<sup>1</sup> on heating either ortho- or para-hydroxybenzyl alcohol for some considerable time it is first converted into a soluble and fusible primary resin, which changes further into an infusible, insoluble final product, thus instancing all the steps which characterize resin formation.

Apart from the character of a material mixture, which is in many cases alone amply sufficient to endow the artificial products with "resin" characteristics, the effects of solvation, enlargement of size of molecule, association, polymerization and colloid conditions, naturally all play a part. These are all, in a sense, additional causes, which increase the degree

<sup>1</sup> *Angew.*, 25, 1946 (1912).

of stability of the resinous condition, which is in any case usually sufficient, but which more particularly ensure the endowment with particular properties. They fulfil a purpose if the comparatively simply primary resins conform to the necessary conditions for further transformation into intermediate and end-products, but may, by association and so forth, also convert an otherwise homogeneous system into a mixture when certain limiting concentrations are exceeded.

The parallel between natural and artificial products is completed by the circumstance, that the latter include materials in which the transformation into resin is similar in character to the analogous process in the case of Japan lac, that is to say, the stage of primary resin is, in a sense, omitted, and the end-product is at once formed. As an example of an artificial product of this character, we may cite the glycollic esters of vinylacrylic acid which, under similar conditions to the fatty drying oils, which have already been compared to Japan lac, can be converted into a solid, resin-like substance of insoluble character. The highly unsaturated hydrocarbons of the butadiene and other similar series also frequently possess the property of being convertible into resinous products which are also frequently of colloidal character, and in these cases also there is frequently no intermediate formation of any soluble or fusible product.

Consideration of the special causes for the resinous character of specific natural and artificial resins certainly indicates that there can be no question of any typical distinction between the two classes of products.

## CHAPTER V

### THE RELATIONS BETWEEN RESINOUS CHARACTER AND CHEMICAL CONSTITUTION

WE have already mentioned (Chapter IV) that in consequence of its definitely physical character, the resinoid state is only indirectly connected with the chemical constitution of the substances concerned. Although, therefore, no such definite relationship exists as in other cases, where it is direct, and where a "typical group" plays a dominant part, the influence of chemical composition can by no means be ignored. It is, therefore, desirable to investigate these relationships.

The preceding considerations have repeatedly drawn attention to the very great influence exerted by suitable admixture of substances on the production of the resinoid condition. If it were merely a question of a mixture as such, it is evident that any mixture whatsoever of organic substances would produce a resin, which is, of course, not the case. Certain necessary auxiliary qualities must, therefore, also be present, which enable the individual constituents to interact. We have already explained in detail that the capability of the system as a whole to form a solid solution or supercooled melt, and to persist in this state, must be considered as a result of the required auxiliary qualities, and these must, therefore, necessarily partake of the character of solubility or fusibility relationships.

These properties must obviously be associated with the individual components of the mixture, and must be present to a sufficient minimum degree to ensure resinoid conditions, although it is preferable that such properties should be available in ample degree.

The so-called miscibility of two or more substances which is requisite, presupposes that at least one of the components is fusible, and that when melted it acts as a solvent of the other components. If this property is shared by more than one component, and if the solvent action of the various melts is

mutual, this must be considered as a particularly favourable circumstance, as by this means the occurrence of zones of mutual insolubility is avoided. Moreover, if the mutual solubility of the melts is well developed, one may be certain that the condition of a solid solution or supercooled melt which is established on lowering the temperature sufficiently will be correspondingly stable, a condition which will also be favoured by the circumstances referred to earlier. (See page 21, *et seq.*)

The required conditions of admixture may be expected to a favourable degree if the main constituents are of chemically allied character, as mutual solubility attains a maximum when solute and solvent are of similar chemical composition. Of course, the necessary conditions may quite well also be fulfilled with mixtures of chemically dissimilar constituents, but in such cases considerable fields of mutual insolubility may be expected. Such possibilities represent a definite menace to the stability of the resinoid condition.

Resins which are, in a sense, homogeneous, such as normal natural secretions and artificial products produced by a typical reaction, actually and demonstrably fulfil the condition which has just been described as favourable, of consisting essentially of chemically similar ingredients, so that this characteristic may be considered to be the rule. It is natural that mixtures which thus comply with the condition of consisting of chemically related components should show a special and far-reaching external similarity, on which the particular chemical nature of the material exercises no practical influence. For this reason, it is possible to group together under the designation of resins a number of materials which show the most extreme variations in chemical composition. That which is in other cases effected by a "typical group," namely, the grouping of numerous individuals with almost arbitrary main chemical nuclei to a single chemical class, is in our case effected by what may be described as a "typical admixture" which leads to an equally characteristic physical character. This conception is, of course, of fundamental importance, as it shows that the resinoid condition must merely be considered as a function of the conjunction

of suitable components of a mixture, and that otherwise chemical conditions are requisite merely to the extent that they govern the suitability of the several constituents.

It would, of course, be wrong to deny all importance to the chemical nature of the components beyond the limitations just indicated. Although the conception of a resin undoubtedly entails but very slight chemical limitations, this is not the case when considering those properties on which the technical application of any such product depends, for solubility conditions, chemical inertness, colour, fastness to light, and so forth are, of course, direct results of the chemical character of the components of the material. Moreover, the especially important property of a resin of convertibility into insoluble and infusible final products is directly dependent on its chemical nature.

Although chemical similarity of the components is of fundamental importance, compliance with this condition is only necessary within certain limits. Occasionally, too great a chemical similarity between the components may even constitute a direct disadvantage. This is particularly the case for products which are destined to be "hardened," that is, to undergo further conversion. Were all the components equally reactive during this process, overhardening would result, and would lead to very many disadvantages such as brittleness, tendency to the formation of cracks, incapacity for being worked, and so forth.<sup>1</sup> If, however, certain constituents only take part in the reaction, this leads to the production of a framework within which the unchanged components, or those which remain in the earlier stages, are distributed. In order to achieve the advantages arising out of these conditions, namely, increased elasticity and high mechanical strength and hardness, the components of the framework must possess a certain degree of solvent and gelatinizing capacity. Products of too different a chemical character do not always display these qualities to a sufficient degree, whilst accompanying constituents of the more chemically active components, which are

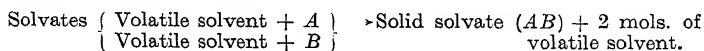
<sup>1</sup> This case actually occurs, for example, in the case of certain phenol-formaldehyde products. It is prevented by the addition of substances of differing character, which are themselves inert under the conditions of reaction.

of similar chemical nature, such as isomers or homologues, almost always possess properties favourable to the purpose. To the extent, therefore, that the reactivity of the various representatives of a group of chemical similar components varies, which may almost always be assumed, chemical similarity of the components of the mixture is a specially favourable factor.

Fundamentally, this is equivalent to the utmost possible tendency to solvation, the importance of which for the production of resinoid characteristics has already been emphasized. As any solution process, whether in an ordinary liquid or in a melt, always implies solvation, the components of the resin must possess properties which favour this process. Solvates may be considered as molecular compounds, the formation of which postulates a sufficient polarity of the interacting individual molecules. Such a process, of course, readily takes place between molecules of similar chemical character, but as indicated by the varying solubility of any one substance in various solvents, considerable limitations usually exist which are at least diminished if solvent and dissolved substances possess groups in common, which is always the case to a greater or less extent in the case of substances which are similar in chemical character.

It is, therefore, not a mere accident that artificial resins are most usually formed in cases in which the possibility of the formation of isomers and homologues exists.

Solvate formation within a resin may take place in two ways, either by melting and subsequent cooling, or by solution of all the components in a volatile solvent which is subsequently evaporated. The former process plays a part in the production of artificial products such as colophony and artificial resins, whilst the latter is the controlling factor in the formation of films. In this latter case, the conversion of the solvate containing the volatile solvent into the solvate of solid consistency must be conceived as a simple replacement. If A and B are the components occurring as a solvate in the solid resin, the process proceeds simply as follows—



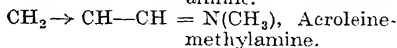
The formation of associated complexes, such as  $(A_xB_x)$ , is practically identical with that of solid solvates, such as  $(AB)$ ; the essential condition is the existence of unsaturated characters, to such an extent at least as to enable components which are apparently saturated to interact with formation of molecular complexes. Such a power of association may even be considered as typical of the resinoid condition, as, in fact, the occurrence of several complexes, which are associated to a variable extent, is alone sufficient to fulfil all the requirements for the development of resinoid characteristics. As a typical example we may cite cellulose acetate, which exists in the monomolecular condition in 0.1 to 0.6 per cent solutions in glacial acetic acid, and then passes through all stages of association to form association-colloids.<sup>1</sup> It is to be noted that in this case we are dealing with what is, in the usual sense, a saturated system. We are, therefore, all the more justified in expecting similar phenomena to occur when dealing with complexes which are unsaturated in the ordinary sense, in virtue of their chemical structure. In practice, all processes for the production of artificial resins are based on the production of mixtures of substances of more or less unsaturated chemical character. This is manifested in the power of association of the components of artificial resins, which can in many cases be carried further with production of higher polymerides. (Plastic masses.)

The view has recently been discussed, based largely on the communications of W. Herzog and I. Kreidl,<sup>2</sup> that the resinoid condition is due to the presence of special resinophoric complexes, more particularly the following—

AZOMETHINE GROUP—



e.g.  $C_6H_5 \cdot N=CH_2$ , Anhydroformaldehyde-aniline.

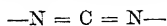


<sup>1</sup> K. Hess and G. Schultze, *Ann.*, 455, 81 (1927). According to K. H. Meyer and H. Mark, *Ber.*, 61, 612 (1928), however, the crystallizable acetyl-celluloses in question represent degradation products. The above considerations are not, however, affected by this fact.

<sup>2</sup> *Oestr. Chem. Ztg.*, 24, 76 (1921), 29, 216 (1926); *Angew.* (1922), 465, 641; (1923), 471; *Chem. Ztg.* (1925), 119; Ger. Pat. 397,603; *Metallbörse*, 16, 2241, 2279 (1926); 18, 229, 287 (1928).



## CARBODIIMIDE GROUP—

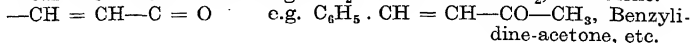


e.g.  $R \cdot N = C = NR$ , Carbodiarylimidene.

## CONJUGATED LINKAGE—



e.g.  $CH_2 = CH-CH = CH_2$ , Butadiene.



e.g.  $C_6H_5 \cdot CH = CH-CO-CH_3$ , Benzylidene-acetone, etc.

In fact, numerous substances which possess the above-mentioned groups do form resins under suitable conditions, probably mainly through the occurrence of polymerization processes. It should, however, be noted that the original substances, such as those cited as examples, are not resins, in spite of undoubted "resinophoric" grouping. It is not, therefore, the presence of the group as such, which must be considered to be decisive, but rather the capacity for reacting in a certain sense. This was recognized by A. Eibner himself,<sup>1</sup> and for that reason he proposed the term resinogene for the groups in question, whereas the term "resinophor" was reserved for the structural elements actually present in the completed artificial resin or in similar materials.

In order to obtain any clear conception of the relations between capacity for resinification and chemical constitution, it is necessary to realize that the presence of any particular group is in no way responsible for the resinoid condition. Therefore, the distinction recently proposed by A. Eibner and E. Koch,<sup>2</sup> between "pseudo-resinophoric" and "resinophoric" groups cannot suffice in order to distinguish between a type of resin capable of crystallization (pseudo-resinoid condition), and a true type of resin (resinoid condition) in a really characteristic manner. Even the discovery that polymerization of substances containing resinophoric or resinogenic groups may lead to crystallized products does not permit of further generalized conclusions with regard to the occurrence of pseudo types and normal types. It is on the contrary necessary to insist that the resinoid state represents the physical expression of the character of the above-described "typical mixtures."

Bearing this fact in mind, it will be realized that the essential point of the observations of Herzog and Kreidl is that

<sup>1</sup> *Angew.*, 36, 33 (1923).

<sup>2</sup> *Angew.*, 39, 1514 (1926).

substances containing the so-called resinophoric or resinogenic groups are frequently, but by no means always, capable of reacting to form resins, that is, mixtures of a certain typical character. The reactive groups themselves are, however, changed in consequence of the occurrence of the reactions which always occur, and which need not necessarily be polymerizations<sup>1</sup> and are, therefore, not present in the resin itself. Therefore, they can obviously exercise no further influence on the character of the reaction product. Even should their reactivity be unexhausted at any stage of resin formation, although resin has already been formed, as is quite possible, neither they nor the transformed structural elements are the true carriers of the resinoid condition; at most, they endow the product in question with the capacity for further transformations, for example, of conversion into end-products.

It would be mistaken to undervalue the views of Herzog and Kreidl because the resinophoric groups are of but limited importance. Even though polymerization may be altogether absent, or may on occasion lead to the production of crystallizable products, this is by no means usual,<sup>2</sup> and, therefore, the relationships between capacity for resinification of substances possessing polymerizable groups and this particular constitution may serve as a valuable guide in practice. If, therefore, the production of a substance containing a resinophoric group may be anticipated by means of any preliminary reaction, such as condensation of an amine with an aldehyde, one may assume with a high degree of probability that this will not be formed in the chemically pure condition, but in the form of a complex mixture (produced by numerous by-reactions), and will, therefore, form a resin, always on the assumption that the conduct of the reaction is chosen accordingly.

Many substances containing resinophoric groups are, in a sense, predestined to form particularly valuable final products, which are insoluble and infusible and manifest resinoid

<sup>1</sup> In the majority of the cases cited by Herzog and Kreidl it is possible that the by-reactions are of predominant importance. (See p. 103.)

<sup>2</sup> The formation of a mixture of monomeric and dimeric products is sufficient to lead to the further production of a resin.

characters, and many examples of this nature might be cited. Certain rules must be taken into consideration, which may be deduced from the behaviour of substances containing unsaturated groups which lead to polymerizing reactions. (See pages 130 *et seq.*)

Finally, the Herzog-Keidl theory enables plausible views to be formulated regarding the course of the transformations undergone by many substances of non-resinoid character into a species of end-product without intermediate formation of the soluble and fusible normal intermediate phase. Amongst natural products this description applies to Japan lac. In the absence of adequate knowledge of the actual constitution of the  $-C_{15}H_{27}$  side-chain of urushiol, with its resinophoric or resinogenic groups, it is only possible to speculate on the course of the reaction; but the processes of film-formation from the fatty drying oils can be more closely followed, and are found to indicate a remarkable dependence on the constitution of the glycerides in question.<sup>1</sup>

<sup>1</sup> J. Scheiber, *Farbe und Lack* (1926), 295; (1927), 75; *Chem. Umschau*, 34, Part I (1927); *Angew.*, 40, 1279 (1927); see also A. Eibner, *Farbe und Lack* (1926), 378, 403.

## CHAPTER VI

### THE LEADING PRINCIPLES OF RESIN PRODUCTION

THE necessary requirements for the production of typical mixtures of the character of a resin are present in an extremely large number of cases, as one can almost always arrange the conditions so that a reaction proceeds, not uniformly, but in more or less numerous directions. By rational regulation of the working conditions one can promote the formation of isomeric and homologous reaction products, and by the deliberate promotion of by-reactions one can induce the required multiplicity of reaction products.

These methods apply to almost all organic substances, if they are subjected to sufficiently effective conditions of reaction. For this reason numerous technical processes, which are in no way intended as sources of resin, lead to the formation of resinous materials as by-products. This applies particularly to almost all processes of purification of relatively non-volatile substances by so-called distillation. In consequence of the concentration of by-products already present, together with the destructive decomposition, more particularly cracking, of the distillable portions, pitches and artificial bitumens or asphalts are formed, which are in all essentials resins.

Such processes are not, however, used for deliberate resin manufacture, which is carried out by processes in which the raw materials are deliberately subjected to such treatment as will produce resin as the practically exclusive product. The methods ordinarily employed for this purpose are resin-producing polymerizations and condensations, which are frequently employed jointly or consecutively.

**Resin-forming Polymerizations.** We have already noted in the preceding chapter that polymerizations seldom take place uniformly, or result in crystallizable products. Moreover, by suitably modifying the conditions one can influence the course of the reaction at will within wide limits, so that one can to

a great extent ensure the production of resin. In addition, one can support the tendency of many polymeric products to autoxidation, for example, by blowing air through the material.

The conditions are naturally most favourable from a technical standpoint when the measures necessary to promote the reaction are not especially violent. As, with few exceptions, dark products are undesirable, it is important to avoid anything which promotes discoloration. The number of technically possible raw materials is, of course, much restricted by such considerations and also by considerations of price and availability, and the field of choice is therefore comparatively narrow. For further details, see pages 52 *et seq.*

**Resin-forming Condensations.** In view of the necessity of obtaining products of as complicated a character as possible, the technique of carrying out a resin-forming condensation for the purpose of resin manufacture is directly opposed to that employed for ordinary preparative purposes. The requirements regarding the character of the resultant product lead to the use of methods of the least possible violence compatible with the required result. As these conditions are most easily realized with such reactions as, in any case, pursue a multi-directional course, such reactions are utilized whenever possible. The use of mixtures of isomers as a raw material offers a further means for increasing the complexity of the resultant resin.

There are, of course, considerable difficulties in so regulating the course of the reaction that a uniform product is always obtained. In particular, much care must be taken in the choice of catalytic agent, as on this the obtainable effect very largely depends. The size of the batch and the method of carrying out the reaction are also of great importance.

It is, therefore, not surprising that certain typical condensations, such as those between phenols and aldehydes, can be carried out in an almost innumerable variety and are constantly yielding new results.

Those condensation processes are of special interest, which first lead to the production of soluble and fusible primary

resins containing complexes susceptible to further polymerization or association, leading to molecules of greater size and which can, therefore, be converted into colloidal final products.<sup>1</sup> In these cases the control of the operation is naturally exceptionally difficult, particularly when the reactions are of an exothermic character. In the case of such reactions the design of the apparatus, method of operation, and so forth are of fundamental importance. For further details, see pages 133 *et seq.*

<sup>1</sup> With regard to the fundamental principle, see K. H. Meyer and H. Mark, *Ber.* 61, 613 (1928).

## CHAPTER VII

### SUBDIVISION AND SCOPE OF THE SUBJECT

IT is rather difficult to define the scope of the class of artificial resins. One would, perhaps, be partially justified in including the transformation and processed products of natural resins, such as hardened resins, esterified resins, autoxidized products, sulphided resins, and other products which can be obtained by combined chlorination and hydroxylation of natural resins.<sup>1</sup> A similar view might be taken with regard to chlorinated fatty oils and rubbers and faktis. Moreover, nitrated, autoxidized and chlorinated bituminous and asphaltic materials, and the products obtained from them by combined processes, may also in a sense, be considered as resins, particularly if pitches, such as "artificial asphalts," are used as raw materials. Artificial bituminous compositions have also, of course, a claim to be included. It cannot, however, be denied that all these products differ essentially from those purposely produced by synthetic processes. The difference consists in the circumstance that by the artificial process the resinous condition is actually produced, whilst in all the cases just mentioned the raw materials are already substances which comply more or less closely with the qualities associated with resins. It therefore appears entirely justifiable to include in the expression "artificial resin," those substances only which are obtained by the treatment of non-resinous raw materials, and to exclude the others mentioned above under the term of "prepared" or "treated" resins. On these grounds the present work has been restricted to the consideration of the production of true synthetic artificial resins only.

With regard to the cellulose esters, their very close relationship to the artificial resins is certainly unquestionable, but it should be borne in mind that the peculiarities of these materials have not really been produced artificially, but are due to the

<sup>1</sup> See the views of Bottler, *Kunstharze*, Munich (1919), p. 7.

structure of cellulose itself. From this standpoint one should consider the cellulose esters as transformation products of a material in which the fundamental conditions for the occurrence of the resinous condition are already latent, and are not, therefore, created by artificial interference. For other additional reasons it is advisable to deal with the cellulose esters as a separate group of substances, and therefore to omit them when dealing with the artificial resins.

On the basis of the standpoint which has just been developed, the recognized important processes of production of artificial resins are divided in the following chapters, into two main subsections, namely—

I. Resin-forming polymerization processes.

II. Resin-forming condensation processes.

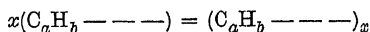
Finally, those artificial resins which are at present of the most technical importance are described in the concluding chapters.



## CHAPTER VIII

### RESIN-FORMING POLYMERIZATION<sup>1</sup>—THEORETICAL

THE term "polymerization," denotes those processes, mostly reversible, in the course of which a more or less considerable number of similar molecules unite to form larger complexes. In distinction to condensation, polymerization does not, therefore, involve the separation of any substance such as water, alcohol, etc. Consequently, the starting product, or monomer, and the reaction product, or polymer, have both the same percentage composition. The process may be expressed by the general equation—



The degree of polymerization, that is, the magnitude of  $x$ , may vary within very wide limits. Both slightly polymerized products, produced from 2, 3, 4, etc., molecules (dimerides, trimerides, tetramerides, etc.), are known, and higher polymers in which  $x$  equals 10, 20, etc., and also in some cases extremely complex aggregates containing 100 simpler units or more. Substances of the last-mentioned type are naturally in many cases very different in character from the less polymerized modifications; more particularly, they usually possess the characters of typically colloidal substances and are, in addition, usually infusible.

It is often possible to convert polymers by suitable means, such as heat, light, or catalysts, into the simple basic complex, or into less highly polymerized substances, a process known as depolymerization. There are also, however, irreversible products, which decompose in other directions under the influence of depolymerizing agents.

A sufficiently marked degree of unsaturation is a necessary condition for any polymerization. The usual structural

<sup>1</sup> See H. Meerwein, "Polymerization und Depolymerization," in Second Volume of J. Houben, *Die Methoden der organischen Chemie*, Third Edition (1925), pp. 593-639.

formulae do not always give a true picture of these conditions. Thus, apparently saturated complexes may be sufficiently active, in consequence of sufficiently strong residual fields, to undergo conversion into polymers containing less energy. On the other hand, the presence of structural elements which are generally recognized as unsaturated does not in any way necessarily denote that polymerization can actually be effected.

There is no doubt that the degree of reactivity in any particular case, or sensitiveness in the sense of effective polymerization, is a function of the total structural relations; but only very conditional generalizations can be made regarding the effective factors, as it is difficult to apply really equivalent experimental conditions even to members of a homologous series or to other closely allied compounds. All polymerizations are very exceptionally sensitive to external influences, and more particularly to heat, light, all kinds of catalysts, and so forth, the quantitative comparison of which from case to case is scarcely possible. Thus, for example, it is in no way sufficient always to work under the same conditions, as in consequence of the variation from substance to substance of specific heats, boiling and melting points, viscosities, absorption ratios, solubilities, and so forth, the conditions would have to be rigorously readjusted from case to case, which could certainly not be achieved to a sufficient degree by constancy of temperature, light source and character and quantity of catalyst. As, moreover, no methods are available for the required measurements of these conditions, one has to be content for the present with qualitative observations as to whether a particular substance is polymerized easily or with difficulty, and whether it is mainly obtainable as a polymer of relatively small or large molecular weight. It is always necessary to bear in mind that the method of investigation regarding the capacity for polymerization of a substance depends principally on the question, whether the specific agencies which promote the polymerization in question are already known or not.

Owing to the fact that many polymerizations are reversible

reaction products of homogeneous composition are not usually to be expected, but on the contrary a condition of equilibrium will usually be attained, with production of a mixture of the starting material with products which are polymerized to various degrees. Under these circumstances, by varying the conditions it may, of course, prove possible to displace the equilibrium in favour of a particular polymer, which may thus be obtained in a more or less pure condition. It is, however, equally possible to exceed the limiting conditions for the formation of any of the polymers, in which case the monomeric starting material will be re-formed. It must be borne in mind that the limits of stability depend to an extraordinary degree on the choice of the polymerizing agent. For this reason the results obtained with varying polymerizing agents are in no sense comparable.

Regarding the mechanism of processes of polymerization, it should be noted that molecules provided with an excess of energy may unite to form complexes of lesser energy in various ways.

The character of the process which actually occurs depends mainly on the structural relations which cause a limitation or extension of the transformations. The results also vary according to the exciting agency.

**Association.** Molecules which are saturated from the structural standpoint, but which, nevertheless, retain residual fields, form polymers comparable to molecular compounds and which share the peculiarities of these.<sup>1</sup> They possess, more particularly, a more or less marked tendency to re-formation of monomers under the influence of solvents. Whilst ordinary molecular compounds are constructed from varying constituents, the substances which we are now considering consist of forms of association of the same fundamental complex. The influence commonly exercised by special solvents on the degree of such associations is clear from the fact that molecular weight determinations in varying solvents give varying results,

<sup>1</sup> See *Chemie in Einzeldarstellungen*, edited by J. Schmidt, X, XXXX, Vol. II; P. Pfeiffer, *Organic Molecular Compounds*, Second Edition, Stuttgart, 1927; R. Kremann, *Restfeldtheorie der Valenz*, Stuttgart, 1923.

which are, moreover, largely independent of the concentrations employed, and which deviate to a varying extent from the expected result.<sup>1</sup>

Association is especially common in the case of compounds containing hydroxyl groups, also with cyclic ethers,<sup>2</sup> lactones,<sup>3</sup> and acid anhydrides.<sup>4</sup> The increase of molecular weight may be very considerable. Moreover, the polymers occasionally show certain chemical differences from the simple molecules, although purely physical differences predominate.

The main factor in their behaviour is the degree of resistance to solvents of the associated complexes. If the solubility is normal, that is, if the forces effecting solvate formation are at least partially able to overcome the space-lattice influences which cause the molecular association, no special physical anomalies are apparent, and the chemical reactivity is usually merely weakened, to a degree dependent on the degree of residual association. Cases are, however, known in which solvents are unable to react effectively, a condition which may lead to the formation of colloidal solutions. (Association colloids, see page 76.) In such cases the concentration may play an important part, in the sense that at great dilution, or within certain degrees of solution, true solutions may be formed, which contain monomolecular, or at least only slightly associated complexes. If, however, one concentrates such solutions, or passes above or below the limiting concentrations in other cases, the association colloids are re-formed.<sup>5</sup>

The relations which we have just discussed are particularly important in the case of resins. Thus it can scarcely be doubted that the so-called micellae of cellulose, which are to be considered as the structural elements of the crystallites, represent

<sup>1</sup> See Meyer and Jacobssohn, *Lehrbuch d. org. Chemie*, Second Edition, Vol. I., 1, 43.

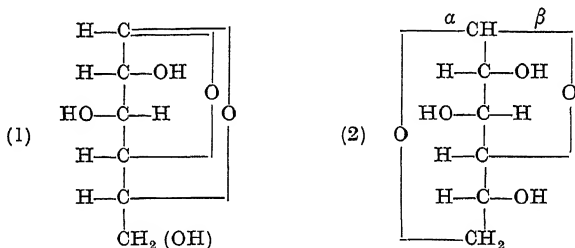
<sup>2</sup> L. Kohn, *Monatsh.*, 21, 80 (1900); Bergmann and Ludwig, *Ann.*, 436, 173 (1924); Bergmann and Kann, *Ann.*, 438, 278 (1924), etc.

<sup>3</sup> L. Kohn, *Monatsh.*, 21, 80 (1900); Nowak, *Monatsh.*, 22, 1140 (1901); Fichter and Beisswenger, *Ber.*, 36, 1200 (1903); etc.

<sup>4</sup> Einhorn and Diesbach, *Ber.*, 39, 1222 (1906); *Ann.*, 359, 151 (1908); H. Staudinger and E. Ott, *Ber.*, 41, 2210, 3829 (1908).

<sup>5</sup> This is the case, for example, for acetyl cellulose; see K. Hess, *Kolloidchem. Beihefte*, 23, 96 (1926); see, however, also K. H. Meyer and H. Mark, *Ber.*, 61, 607 (1928).

association-polymers held together by space-lattice influences. The tendency to dissociation of these complexes is extremely small, and for this reason it is only possible to demonstrate the possibility of such dissociation under very definite and limited conditions. Thus, cellulose<sup>1</sup> may be dissociated in copper-ammino solution into molecules of the magnitude of a glucose anhydride; similar relations exist in solutions of acetyl cellulose in glacial acetic acid.<sup>2</sup> Formula 1 for cellulose, which has been proposed by K. Hess, as a result of numerous researches,<sup>3</sup> leads to the assumption that the cause of the extreme stability of the micellar complex is to be ascribed to the presence of oxygen "bridges," as in certain other cases, such as the ethylene oxides<sup>4</sup> and the cyclic acid



anhydrides these must be regarded as the causes of the tendency to association in consequence of incomplete saturation

<sup>1</sup> K. Hess, *Naturwissenschaften*, 14, 435 (1926).

<sup>2</sup> K. Hess, *Kolloidchem. Beihefte*, 23, 95 (1928); see also K. Hess, G. Schultze, and E. Messner, *Ann.*, 444, 279 (1925); K. Hess and G. Schultze, *Ann.*, 448, 101 *et seq.* (1926); see, however, K. H. Meyer and H. Mark, *Ber.*, 61, 606, 612 (1928).

<sup>3</sup> K. Hess, *Kolloidchem. Beihefte*, 23, 98 (1926); see also K. Hess, *Ann.*, 435, 115 (1923); F. Micheel and K. Hess, *Ann.*, 449, 146 (1926). As a result of X-ray measurements the cellulose formula proposed by K. Hess has recently been replaced by a symbol, in which cellobiose chains function as constructional elements of the crystallites. These views do not affect the above considerations in principle, the essential difference being that in place of the relatively simple fundamental complex (Formula 1), the more complicated cellobiose chains appear as carriers of the micellar field of force. See K. H. Meyer and H. Mark, *Ber.*, 61, 593 (1928); see also K. Freudenberg, *Ann.*, 460, 295 (1928); 461, 130 (1928); also H. Staudinger, H. Johner, R. Signer, G. Mie, and J. Hengstenberg, *Ztschr. phys. Chem.*, 126, 425 (1927), on the comparison of the structure of cellulose with that of the polyoxymethylenes. See also p. 63.

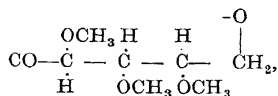
<sup>4</sup> J. Houben and H. Meerwein, *Methoden d. Org. Chem.*, Third Edition (1925), Vol. 2, 637.

of the valencies or of special conditions of molecular stress.<sup>1</sup> However, some other factor appears to come into play which is at present obscure. Thus, for example, the laevoglucosan (Formula 2) which is obtained on heating cellulose to 120° C.<sup>2</sup> also contains two oxygen bridges, as does cellulose itself, but does not show any inclination to form micellar complexes of any kind, as is proved by its easy and regular solubility in water.

The formation of association colloids is especially important in film-formation, as it exercises a considerable effect in promoting the conversion of the original comparatively simple system in solution, at the critical moment, into a mixture of complexes of similar character which are also mutually soluble.

Association also exerts an important influence on the behaviour of shellac. It is known that lactones and lactides frequently show an inherent tendency to polymerization, as may be concluded from the behaviour of  $\delta$ -valerolactan,<sup>3</sup> the non-existence of monomeric salicylic acid lactone,<sup>4</sup> and the easy formation of polyglycollide.<sup>5</sup> According to the investigations of C. Harries and W. Nagel,<sup>6</sup> shellac resin belongs structurally to the lactide class, and a tendency to polymerization of the association type, or to aggregation is, therefore, not surprising. The methods which are found necessary in order to reconvert the product insoluble in alcohol into the form soluble in that liquid are essentially such as might be

<sup>1</sup> *Loc. cit.*, 639; H. D. K. Drew and W. N. Haworth, *J. Chem. Soc.* (1927), 775, deny that unsaturated valencies of the oxygen bridge are a cause of molecular association in the case of 2, 3, 4-trimethyl-1-arabonic acid lactone



which is polymerized by traces of acid (*M.*, 1900 to 2100).

<sup>2</sup> Regarding this formula, see K. Hess, *Kolloidchem. Beihefte*, 23, p. 98, footnote 2 (1926); on the basis of the new glucose formula of W. N. Haworth, *J. Chem. Soc.*, 129, 89 (1926) the  $\beta$ -oxygen bridge would be in the 1-5 and not in the 1-4 position.

<sup>3</sup> See footnote, ‡ p. 54

<sup>4</sup> See von Richter and Anschütz, *Kohlenstoffverbindungen*, Eleventh Edition, Vol. 2, 322.

<sup>5</sup> Under the influence of a trace of zinc chloride.

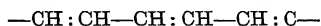
<sup>6</sup> *Wiss. Veröff. Siemens. Konz.*, III, 2, 12 (1924); *C.* (1924) II, 1187.

expected in order to resolve the space-lattice association.<sup>1</sup> The very surprising stability of the converted resin to hydrolytic influences, which can be overcome in a similar manner to the insolubility in alcohol, has been explained by Harries and Evers<sup>2</sup> as due to the exceptionally far-reaching saturation of the aggregated complex.

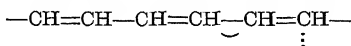
### Polymerization of Chemically Unsaturated Compounds.

Whilst association only occasionally occurs in such a form as to lead to the formation of relatively stable complexes with new properties, the polymerization of chemically unsaturated compounds gives rise to an extraordinary number of substances of all degrees of material alteration, by the structural union of similar molecules.

The condition for a reaction of this kind is the presence of ordinary unsaturated groups, the activity of which is unhampered by intermolecular neutralization of the free valencies. This effect is illustrated by the facts that the trebly conjugated system



is reactive, as in the polymerization of trielaestearic acid glyceride or Chinese wood oil,<sup>3</sup> whilst the same system is practically inert if closed to form a ring, as in benzene. The reason for the difference is to be found in the fact that in the former case the unsaturated valencies are available, whilst in the latter they are not, in consequence of the ring formation.



Free Unsaturated Valencies



No Free Unsaturated Valencies

Just as substances with undoubted double linkages occasionally show no tendency to combine with bromine,<sup>4</sup> so occasional

<sup>1</sup> Treatment with glacial acetic acid or formic acid; also treatment with alcohol containing hydrochloric acid according to Ger. Pat. 421,337.

<sup>2</sup> *Ber.*, 56, 1088 (1923).

<sup>3</sup> On the proof of the presence of the trebly conjugated group in elaeostearic acid, see J. Böeseken and H. J. Ravenswaay, *Rec. Trav.*, 44, 241 (1925); *C.* (1925), II, 107. The objections of M. Ishio, *C.* (1926), I, 3594, are unconvincing; see also the summaries of J. Scheiber, *Farbe und Lack* (1927), 646; (1928), 146; also F. Fritz, *Farben-Ztg.*, 33, 1225 (1927-28).

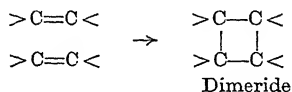
<sup>4</sup> See the Bibliography in H. Meyer, *Analyse und Konstitutionsbestimmung*, Third Edition (1913), p. 936.

absence of polymerizing tendency may be expected in spite of structural unsaturation.<sup>1</sup> On the other hand, under the influence of especially favourable structural conditions the activity of an unsaturated group may be very greatly increased. (See below.)

Thus the conditions are very varied and can, moreover, not always be anticipated. In any event it is not surprising that, apart from the varying tendency to polymerization, the course of the process itself varies greatly.

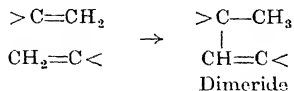
**The Ethylene Double Bond.** For substances with an ethylene double bond the following possibilities exist—

(a) The free valencies are saturated by union of the molecules in pairs, with formation of dimerides with a four-carbon ring, in the following manner—



Unless there are exceptional complications, such as the presence of other unsaturated groups or of complexes capable of association, the reaction product is the final product of a polymerization of the above character. It should be noted that if the groups attached to the carbon atoms of the double band are of dissimilar character, numerous structural and geometrical isomers of the cis- and trans-varieties may be formed,<sup>2</sup> as in the case of the truxillic acids.

(b) The liberation of free energy may occur with migration of a hydrogen atom, as follows—



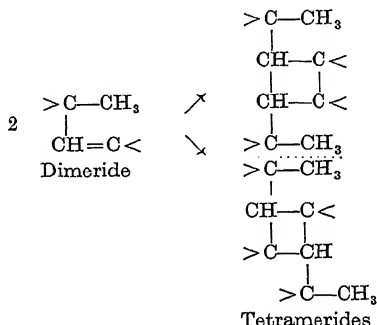
In distinction to those formed by process (a), the products in this case are still unsaturated, as one double bond still remains. A further polymerization in the sense of reaction (a)

<sup>1</sup> See also the following chapter.

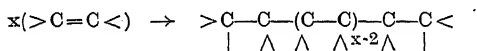
<sup>2</sup> A compilation of the possible cases of isomerism is to be found in J. Houben, *Methoden der org. Chemie*, Third Edition (1923), in the section on "Light Exposure," p. 1397 *et seq.*



may, therefore, occasionally occur. In consequence of alternative possibilities for the formation of a tetrameride in this manner, such a reaction may produce several isomers, which may be regarded as *cis*- and *trans*-forms of 1-2 and 1-3 substituted tetramethylenes—



(c) There is yet another final possibility, in which the number of individual molecules which may unite to form the polymeride has no theoretical limit, namely, the reaction according to the following scheme—



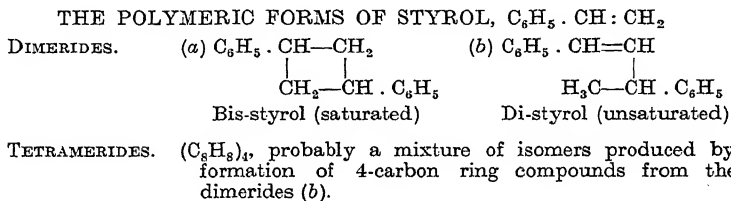
**Higher Polymerides.** This last possibility seems particularly adapted to the explanation of the formation of highly polymerized products, the formation of which may well be of a reversible character. The free valencies of the end carbon atoms, according to H. Staudinger's views,<sup>1</sup> may either remain further unaltered as free end valencies, or may become saturated by ring formation, or addition (for example, of the catalyst), or by migration of hydrogen.

Substances are in fact known which are capable of polymerization in the sense of all the above-mentioned reactions. One of these, which has been investigated with exceptional completeness, is styrol,<sup>2</sup> which has been shown to exist in

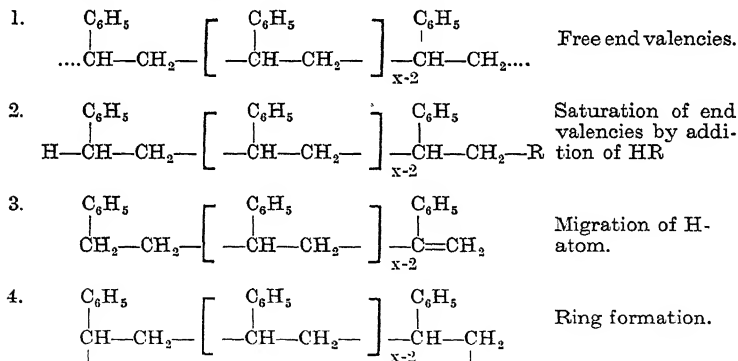
<sup>1</sup> *Ber.* 59, 3035 (1926).

<sup>2</sup> H. Stobbe and G. Posnjak, *Ann.*, 371, 259 (1910); H. Stobbe, *Ann.*, 409, 1 (1915).

two dimeric, one tetrameric, and numerous more highly polymerized forms. As will be seen from the following summary, the two dimerides correspond to cases (a) and (b) above. The tetrameride is probably a mixture. According to Staudinger, the higher polymerides are formed from 20 to 100 and, perhaps, more simple molecules; these must be formed according to scheme (c)



Higher polymerides,  $(C_6H_5)_x$ , with varying magnitudes of  $x$ ; according to Staudinger these are probably formed as follows—



In consequence of the great influence of external factors on the course of a polymerization, it is difficult to foresee in advance which of the various possibilities will be most easily realizable. From the standpoint of the production of artificial resins the highly polymerized products are, of course, of special interest, as with increased molecular weight their character becomes increasingly colloidal, and the possibilities of obtaining insoluble and infusible products increases accordingly. So far as experience goes one may, perhaps, anticipate

that highly polymerized products are only to be expected when the reacting ethylene group is activated by the presence of other negative radicles. Thus, for example, the following substances all possess the capacity for forming highly polymerized products—

$\text{CH}_2 : \text{CH} . \text{C}_6\text{H}_5$	Styrol
$\text{CH}_2 : \text{CH} . \text{CH} : \text{CH}_2$	Butadiene
$\text{CH}_2 : \text{CH} . \text{O} . \text{CO} . \text{CH}_2\text{Cl}$	Chloracetic-vinyl-ester (and similar products) <sup>1</sup>
$\text{CH}_2 : \text{CH} . \text{CH} : \text{CH} . \text{COOH}$	Vinylacrylic acid <sup>2</sup>

and so forth.

Moreover, such systems will have exceptional powers of polymerization to form a variety of compounds, that is, mixtures of comparatively simple and highly polymerized complexes, which is, of course, very favourable to any desired production of resin. As the course taken by the polymerization is very greatly influenced by external factors, these must, of course, receive special attention in such cases. (See, however, pages 69 *et seq.*)

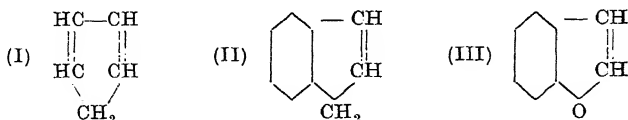
The polymerization of ethylene derivatives is certainly by far the most frequent reaction of this kind. Similar reactions involving double linkages between carbon and oxygen occur comparatively rarely. (See pages 65 and 123.) The association of ethylene and carbonyl groups mainly causes the former group to become more reactive, whereas the latter may facilitate association. When, therefore, Herzog and Kreidl state that the joint presence of ethylene bonds and of the carbonyl group, more particularly in the "resinophoric" complex— $\text{CH} : \text{CH} - \text{CO} -$ , is particularly favourable to resin-forming polymerization, they are certainly justified to some degree. (See, however, pages 98 *et seq.*)

The tendency to polymerization is naturally greatly dependent on the various groups combined with the ethylene radicle. The activity of the ethylenic linkage is sometimes retained even when this forms part of a ring formation, so that highly

<sup>1</sup> See, for example, Ger. Pats. 271,381, 281,287, 281,288, 281,877, 290,544, 291,299, 313,696.

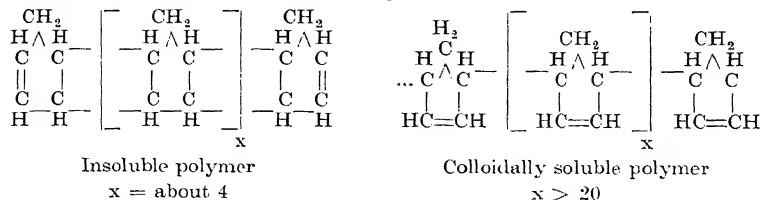
<sup>2</sup> Ger. Pat. 389,086.

polymerized complexes may be formed. This is particularly the case for cyclo-pentadiene (Formula I)<sup>1</sup> and indene (Formula II),<sup>2</sup> whereas cumarone (Formula III) scarcely forms any polymer higher than the tetrameride.



In this connection we must consider the relations which exist between tendencies to polymerization and to autoxidation. In many cases, such as cyclopentadiene, indene, butadiene, and others, an undoubted parallelism exists. It must, however, be remembered that oxygen may act not only chemically but also catalytically,<sup>3</sup> so that complex phenomena may be observed. In some cases, moreover, autoxidation must be considered as preliminary to polymerization, relatively inert systems being activated by the chemical change. This sequence is probably the main factor in the natural drying of fatty oils,<sup>4</sup> and also in the case of other substances such as Japan lac and vinylacrylic acid esters.

<sup>1</sup> Cyclopentadiene polymerizes in two ways. The insoluble product which is obtained on heating is of comparatively low molecular weight and is probably formed from about six molecules only. On the other hand, the polycyclopentadiene obtained with zinc chloride, which forms a colloidal solution, is formed from at least 20 molecules. These facts, which are at first sight remarkable, are explained by the circumstance that cyclopentadiene is able to act in two manners, as either one or both double bonds may take part. In the former case the contraction is considerably greater and the saturation much more complete than in the latter. According to H. Staudinger the relations are expressed by the following formulae—



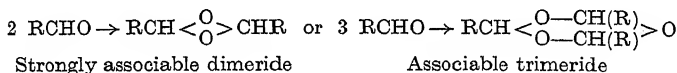
<sup>2</sup> Polyindenes probably contain up to 50 and more monomeric molecules.

<sup>3</sup> See C. Engler, *Report of the Eighth Internat. Congress of Applied Chemistry*, New York, Vol. 25, 661 (1912).

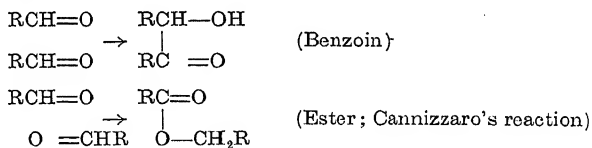
<sup>4</sup> J. Scheiber, *Farbe und Lack* (1926), 295; (1927), 25; *Angew.*, 40, 1279 (1927); compare A. Eibner, *Farbe und Lack* (1926), 378, 403.

In the case of other unsaturated groups there are found, within certain limits, the same kinds of satisfaction of valencies with union of the characteristic complexes, as we have found to be typical of the ethylene group. It is obvious that peculiarities of structure may exert an action and impart secondary characteristic properties to the polymerides.

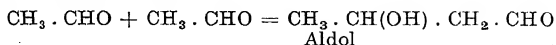
**The Carbonyl Group.** This group is the carrier of polymerizing powers, particularly in the case of the aldehydes; in this case the mutual saturation of valencies is effected either by direct saturation or by hydrogen migration. In the former case dimerides and trimerides are formed, which usually manifest considerable powers of association. These reactions proceed according to the schemes—



The formation of special dimeric forms by hydrogen formation is typical of most aromatic aldehydes and also of formaldehyde. The reaction may occur with formation of either benzoin or esters—



Although the process is in principle the same as with ethylene derivatives, the products are not such as one would ordinarily consider to be polymerides. A similar consideration applies to aldol formation—



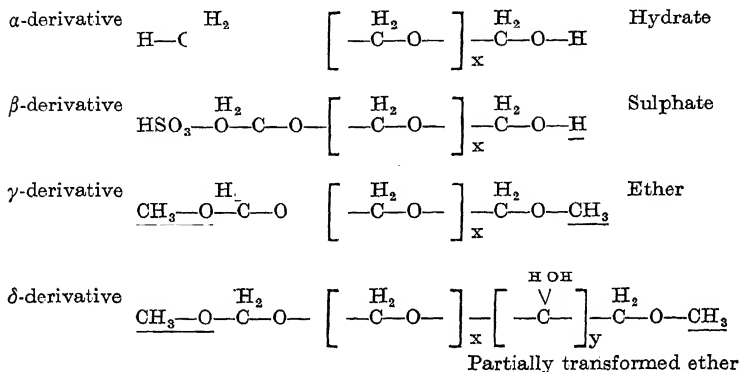
although this case is also not a true condensation.

It is fairly obvious that polymerization may occur in what may be considered a continuous sequence. According to H. Staudinger,<sup>1</sup> this is to be assumed in the case of

<sup>1</sup> *Ber.* 59, 3025 (1926).

polyhydroxymethylenes, the  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  modifications of which may be formulated as follows—

FORMULAE OF THE POLYHYDROXYMETHYLENES  
ACCORDING TO STAUDINGER



These formulae take into account the methods of formation of the various modifications. The  $\alpha$ -products (paraformaldehyde and polyhydroxymethylene) are hydrates. The  $\beta$ -derivative is produced by the action of sulphuric acid. The  $\gamma$ -modification is only formed in the presence of methyl or ethyl alcohol. Finally, the  $\delta$ -derivative is formed from the  $\gamma$ -derivative by treatment with boiling water, which probably leads to partial transformation of the unstable complexes  $\text{---C---O---C---O---}$  into the more stable chain  $\text{---O---C---C---O---}$ .

The *thiocarbonyl* group, which acts as the carrier of tendencies to polymerization in thioaldehydes and even in thioketones, acts in a similar manner to the carbonyl group. The production of trimerides predominates. In the special case of thioformaldehyde, however, polymerization with the formation of a long chain appears to occur.<sup>1</sup>

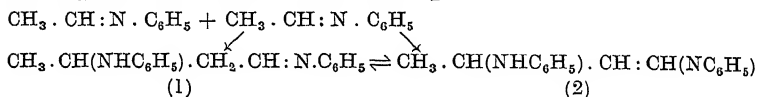
As it is usually impossible to polymerize ordinary ketones, it must be assumed that the thiocarbonyl group is especially

<sup>1</sup> The products appear to be similar to those from formaldehyde; thus, for example, a mercaptan corresponding to polyhydroxymethylene hydrate, and others similarly; see E. Fromm and M. Soffner, *Ber.*, 57, 371 (1924).

susceptible to polymerization, at least in the case of thioketones.<sup>1</sup>

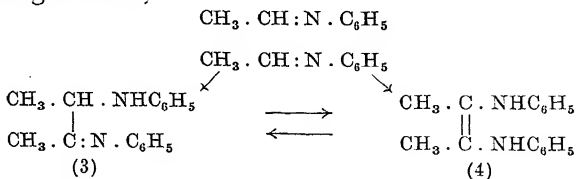
**The Azomethine Group.** This group also shows obvious analogies with the ethylene double linkage.

Thus the alkylidene-anilines (Schiff's bases)  $R \cdot CH : N \cdot Ar$  are themselves very unstable and change spontaneously into dimerides, which occur in isomeric forms.<sup>2</sup> The interaction of the monomeric molecules which occurs in this case must be regarded as a kind of aldol formation, as the products are characterized by easy conversion into quinaldines. On this assumption the reaction must take place as follows—



The compound (1) would be of secondary-tertiary type, and would be capable of anil isomerism; the compound (2), on the other hand, is of di-secondary type, and might show ethylenic isomerism. It is, however, also possible that (1) and (2) are reversibly transformable each into the other.

A. Eibner inclines to the view that the formula (2) must apply to the mutually intertransformable isomers (Eckstein's and Eibner's bases),<sup>3</sup> but the behaviour of these substances can also be accounted for by another method of formation or formulation, if one assumes that combination occurs in the same manner as is indicated in the case of dimeric ethylenic groups. In fact, the union of two monomeric molecules in the following manner,

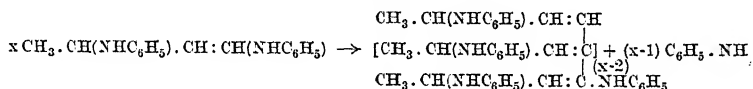


<sup>1</sup> Thioketone is the only member of its class which has been obtained in the monomolecular condition, but polymerizes very easily to the trimeride; see E. Baumann and E. Fromm, *Ber.* 28, 901 (1895).

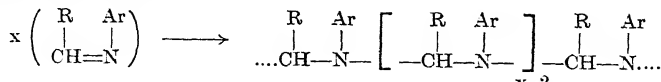
<sup>2</sup> See W. von Miller and J. Plöchl, *Ber.* 25, 2020 (1892); 27, 1927 (1894); F. Eckstein, *Ber.* 25, 2029 (1892); L. Sender, *Ber.* 25, 2033 (1892); A. Eibner, *Ber.* 27, 1299 (1894); 29, 2977 (1896); A. Eibner and F. Peltzer, *Ber.*, 33, 3460 (1900). <sup>3</sup> See *Angew.*, 39, 1515 (1926).

would lead to products which would also show secondary-tertiary (3) or di-secondary (4) characters, and would possess the necessary structure for conversion into quinaldine. For these reasons the formulae (3) and (4), which may be suggested on grounds of analogy, may certainly be considered.

There are, moreover, other reasons for this view. Thus, G. Schultz<sup>1</sup> obtained a resinoid product from aniline hydrochloride and acetaldehyde, which consists, according to A. Eibner and E. Koch<sup>2</sup>, of more highly polymerized complexes. The above mentioned authors incline to the view that this mixture of polymerides is formed from product (2) above, by separation of aniline and subsequent union of the residues:



This assumption is based more particularly on the observation that both isomerides (2) yield quinaldine smoothly on boiling with hydrochloric acid, whilst Schultz's product is unaltered by such treatment, and is only converted into quinaldine when melted with zinc chloride. This is, however, the identical behaviour which might be expected from a polymer formed in the manner of other higher polymers by continued combination of the monomeric molecules in the manner assumed by H. Staudinger in the case of polystyrols and polyhydroxymethylenes:



as the formation of quinaldine requires previous depolymerization, for which purpose the hydrochloric acid, which is actually used as a polymerizing agent in the case in question, would probably not be very suitable<sup>3</sup>

<sup>1</sup> Ber., 25, 1600 (1892).

<sup>2</sup> Angew., 39, 1517 (1926).

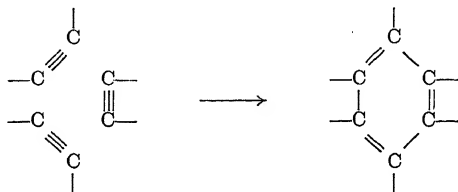
<sup>3</sup> A. Eibner and E. Koch (*loc. cit.*) purified and analysed the resin obtained by Schultz's method and obtained the following results: C, 80.38–81.57%; H, 7.62–7.65%; N, 9.54–9.83%. These figures are entirely in accordance with the formula  $(\text{C}_8\text{H}_5\text{N})_x$  for a polymerized ethylidene-aniline, which has the theoretical composition: C, 80.67%; H, 7.56%; N, 11.76%. The low nitrogen result is not surprising, as by-reactions are not excluded and the purification must necessarily be incomplete.



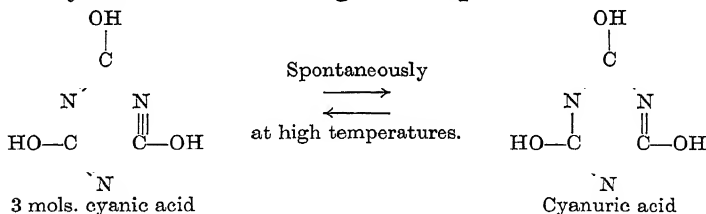
It is, therefore, unquestionable that there is a parallelism in the general behaviour of the ethylene and azomethine groups.

For trebly unsaturated systems, much the same fundamental possibilities exist as for the other characteristic unsaturated groups. Certain of these will now be referred to.

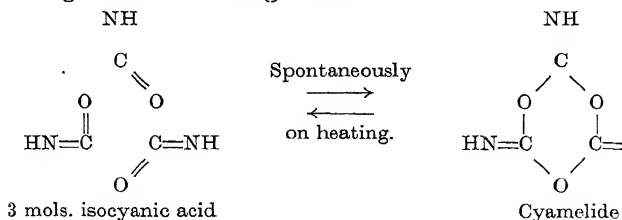
**The Ethine (Acetylenic) Group.** This group usually forms trimerides by simple interaction of the available valencies, with formation of benzene derivatives according to the following scheme—



**The Nitrile Group.** Substances containing this group display a similar tendency to form cyclic systems, which in this case belong to the triazine (Kyanidine) class. Thus cyanic acid forms cyanuric acid, according to the equation—



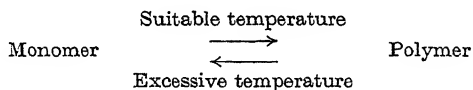
In the tautomeric form of cyanic acid (isocyanic acid,  $\text{HN} : \text{C} : \text{O}$ ) a kind of competition occurs between two groups, the carbonyl and azomethine groups. The course of the polymerization favours the carbonyl group, cyamelide being formed according to the following scheme—



It should be noted that substances containing nitrile groups are particularly prone to react in other than the normal manner.

**Polymerizing Agencies.** The initiation and continuance of almost all polymerizations are to a high degree dependent on external agencies, for which reason it is hardly possible to foresee the probable behaviour of any substance. A further complication is due to the fact that agencies which promote polymerization may also have a depolymerizing action. In some cases this leads to equilibrium conditions, but in others the reaction is thus completely prevented.

**Temperature.** The temperature to which a substance capable of polymerization is exposed is of crucial importance. Pressure also plays a part.<sup>1</sup> It may be said in general terms that heat assists all polymerization, but the temperature rise must not be too great, as otherwise the polymers which are at first formed may be again decomposed.



The conditions vary with the position of the limits of stability. If these are exceeded for all possible polymers the monomer will be re-formed. Otherwise, the reversal of the reactions ceases at that polymer, the limit of stability of which lies just above the temperature employed. Such considerations may explain why  $\beta$ ,  $\gamma$ -dimethylbutadiene forms in the cold, and in the absence of catalysts, a polymeride insoluble in every solvent, whilst at 90 to 100° C. a readily soluble caoutchouc is formed.<sup>2</sup> In the former case the degree of polymerization is far higher, whilst at 90 to 100° C. those products can alone be formed which are stable at that temperature. This is, of course, a case of technical importance.

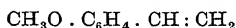
**Light.** The effect of light is almost more difficult to control as, apart from polymerization and depolymerization, it may

<sup>1</sup> W. Stegemann, *Angew.*, 40, 750 (1927). Regarding polymerization under the influence of silent discharge, see N. Prjanischnikow, *Ber.*, 61, 1358 (1928).

<sup>2</sup> See J. Houben and H. Meerwein, *Methoden der org. Chemie*, Third Edition (1925), p. 600.

initiate many other processes if the necessary conditions are present. J. Houben<sup>1</sup> mentions the following of these: photolysis (ionization, deoxidation, dehydrogenation, hydrolysis, and other fission reactions), photosynthesis (oxidation, halogenation, combination, esterification, formation of amides, condensation, etc.), and photomerization (change of configuration, intramolecular transformation, polymerization, depolymerization, etc.). It is, therefore, clear that a complication of processes may occur, which may, of course, considerably affect the character of the result.

The light absorbing properties of the monomer and polymers exercise a decisive effect. According to Grotthus's Law, no photo-reaction can occur unless the wave length of the light which is applied is such as will cause it to be absorbed by the material. Unabsorbed light exerts no action. It is therefore clear that, for example, exposure to sunlight which contains rays of long wave length, will lead to results quite different from those obtained with the mercury lamp, which emits light of short wave length. A classical example of these relationships is furnished by the investigation of H. Stobbe and K. Toepfer<sup>2</sup> on the relation between the polymerization of p-vinylanisol,



and the wave length of the light employed. Whilst in sunlight polymerization occurs smoothly, with formation of a highly polymerized product, when exposed to the mercury-quartz lamp no reaction occurs.

The cause is to be sought in the differing absorption spectra of the monomeric and polymeric forms, which is a quite general phenomenon. The degree of unsaturation is a prevailing factor in the transparency of a substance to light. The stronger the residual fields of affinity, the more definite and selective is the absorption, and when this is thus displaced in the direction of the visible portion of the spectrum it may lead to the occurrence of colour appreciable by the eye.<sup>3</sup> Any diminution

<sup>1</sup> *Meth. d. org. Chemie*, Third Edition (1925), p. 1164 *et seq.* (Section on "Light Treatment.")

<sup>2</sup> *Ber.* 57, 484 (1924).

<sup>3</sup> See H. Ley, *Farbe und Konstitution*, Leipzig (1911), p. 3 *et seq.*

of strength of the residual fields causes corresponding displacement of the light absorption towards the ultraviolet end of the spectrum, whilst at the same time the selectivity is decreased. In every case, therefore, polymerization causes the colour to become lighter, that is, the substance becomes

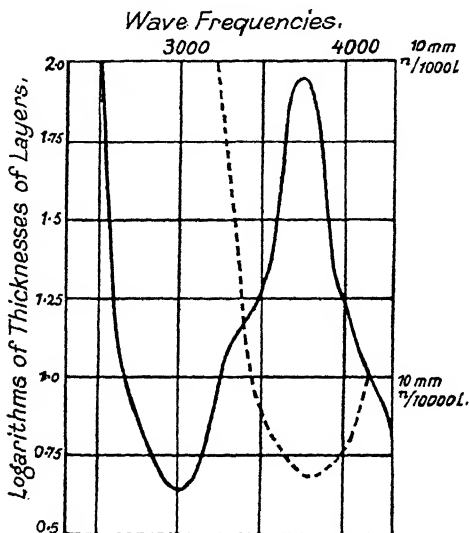
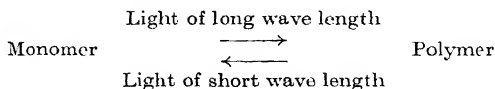


FIG. 2. CHANGE OF ABSORPTION SPECTRA ON POLYMERIZATION

Alcoholic solutions—  
Monomeric cinnamylidene-benzylcyanide  
Photo-dimeric cinnamylidene-benzylcyanide

more transparent. Thus, for example, cinnamylidene-benzylcyanide, which is yellow, forms a colourless dimeride on photopolymerization by sunlight.<sup>1</sup> The changes in the absorption spectra which simultaneously occur, are shown in Fig. 2.

It may, therefore, be anticipated that on photo-polymerization an equilibrium will generally be attained between the monomeric and polymeric forms.



<sup>1</sup> H. Stobbs, *Ber.* 45, 3398, 3403 (1912).

In special cases, in which the differences between the absorption spectra are well marked, it may be possible to determine limits of wave length, on exceeding which the photo-equilibrium is displaced in one direction, whilst on decreasing it the reaction proceeds in the opposite direction. Such a case actually occurs with p-vinyl-anisol, the monomeric form of which absorbs light of long wave length only, whilst the polymeric modification absorbs light of short wave length only. In this case the limiting wave length is  $330\ \mu\mu$ .

It is further to be expected that amongst several possible products of photo-polymerization the character of the light employed may lead to a selection, which case will occur if the system is exceptionally variable, as, for example, in the case of cinnamic acid.<sup>1</sup>

The course of a photo-polymerization may, of course, be affected by heating, but is affected especially strongly by the addition of catalysts such as acids or iodine. In the case of certain photo-polymerizations definite indications of the formation of autocatalysts have been observed.<sup>2</sup>

**Catalysts.** Catalysts exercise a very great influence on polymerization processes, and the behaviour of a very large number has been investigated. Their action varies from case to case, so that it is impossible to generalize from the results of individual experiments. With this limitation, it has been found that the substances shown on page 73, can be used.<sup>3</sup>

The action of the various additions is sometimes selective, that is, leads to the formation of a definite polymer. The effect of a catalyst is assisted by heat. In consequence, however, of the ease with which the limits of stability of certain polymers are exceeded, the result obtained on raising the temperature is often quite different from that at ordinary temperature. It should also be noted that even in the cold a catalyst displaces the limit of stability in a downward

<sup>1</sup> See the summary of the experimental results obtained in J. Houben, *Methoden der org. Chemie*, Third Edition (1925), p. 1289 *et seq.*

<sup>2</sup> See H. Stobbe and K. Toepfer, *Ber.*, 57, 489 (1924); see also H. Stobbe and G. Posnjak, *Ann.*, 371, 286 (1909).

<sup>3</sup> See J. Houben and H. Meerwein, *Methoden der org. Chemie*, Third Edition (1925), pp. 602, 603; H. Staudinger and H. A. Bruson, *Ann.*, 447, 110 (1926). The list makes no claim to completeness.

direction. Thus, according to Staudinger,<sup>1</sup> styrol undergoes the same polymerization in the cold in the presence of tin tetrachloride as it does at 270° C. without that substance.

## ACIDS—

Hydrochloric acid  
Sulphuric acid  
Glacial acetic acid  
Sulphuric acid mixed with glacial acetic acid  
Sulphuric acid mixed with acetic anhydride  
Phosphoric acid  
Picric acid  
Sulphurous acid

SALTS AND SALT-LIKE COMPOUNDS—<sup>2</sup>

Boron halides (fluoride, chloride, iodide)  
Aluminium chloride  
Ferric chloride  
Tin tetrachloride  
Titanic chloride  
Zinc chloride  
Sodium and potassium acetates

## METALS AND NON-METALS—

Sodium, potassium  
Aluminium  
Iodine (and potassium tri-iodide)  
Sulphur

## METAL-ORGANIC COMPOUNDS

## PHOSPHINES

## ORGANIC BASES—

Pyridine  
Piperidine

## VARIOUS—

Water  
Ozonides  
Superoxides  
Certain silicates (floridine, fullers' earth)

*Negative catalysis* is sometimes observed, that is, the absence of any action, even though this would normally occur spontaneously. This effect may more particularly be obtained on adding iodine, sulphur,<sup>3</sup> or especially phenols.<sup>4</sup> In general, those substances seem particularly susceptible to negative catalysis, which are autoxidizable, such as styrol, acrolein, and vinyl derivatives. Possibly the very striking action of such additions is due to prevention of the formation of an auto-catalyst, the presence of which is essential to the initiation of a polymerization, and to which it is fairly probable that the character of a peroxide may be ascribed.<sup>5</sup> It is worth noting that the same factors which prevent polymerization in the case

<sup>1</sup> *Ber.*, 59, 3031 (1926).

<sup>2</sup> According to W. Stegemann, *Angew.*, 40, 750 (1927), in the case of metal halides the nature of the electronic shells plays a decisive part. The action is therefore greatest if the atomic linkage is homopolar, as in the case of boron-fluoride, as the possession of one or more electrons by two atoms in common, which is characteristic of such linkages, makes the electronic shells metastable.

<sup>3</sup> Krakau, *Ber.*, 11, 1261 (1878).

<sup>4</sup> Ch. Moureu and Ch. Dufraisse, *Compt. rend.*, 169, 1068 (1919); 170, 26 (1920); C. (1920), I, 771; British Pat. 181,365; Ger. Pat. 340,871.

<sup>5</sup> See J. Houben and H. Meerwein, *Methoden d. org. Chemie*, Third Edition (1925), p. 604.

of the above-mentioned substances, also prevent the drying of those fatty oils in the case of which an easily polymerized system can only be developed by means of oxidation processes, such as linseed oil and poppy oil.<sup>1</sup> As in the natural drying of oil autocatalytic action also plays a part, and is probably promoted by peroxide complexes,<sup>2</sup> the parallelism between the two cases is complete.<sup>3</sup>

**Detection of Polymerization.** The occurrence of polymerization can be easily and certainly detected by a number of phenomena. Apart from the lightening effect on the colour, already referred to, and due to reduced light absorption, numerous other typical changes occur. Thus liquid monomers show on polymerization, rise of boiling point, increased density, increased index of refraction, reduced dispersion and more particularly increased viscosity, which may proceed so far as to produce solidification. Solid monomers show on polymerization, rise of melting point and reduced solubility. These changes are accompanied by changes in the chemical properties, more particularly reduction of the iodine value, reduced power of absorbing hydrogen and reduced tendency to autoxidation.

Obviously, polymers must be of increased molecular weight, the determination of which is, however, often very difficult. The determinations are only reliable, more or less, in the case of relatively low polymerides, and it is impossible to state at what point they cease to be reliable. In the case of highly polymerized or, and more particularly, of exceptionally insoluble substances, the usual methods obviously fail, as they also do in the case of colloids. Within certain limits, however, useful results can even be obtained in these cases by depolymerizing the original molecule to such a degree that regularly soluble products are just obtained. Suitable reactions for such a purpose must, of course, be discovered in each case. According to a summary by H. Staudinger<sup>4</sup> of his own work and

<sup>1</sup> J. Scheiber, *Farbe und Lack* (1927), 26, 600.

<sup>2</sup> A. Eibner, *Fette Oele*, Munich (1922), p. 53 *et seq.*

<sup>3</sup> Molecules of  $O_2$  are very probably liberated; see J. Scheiber, *Farbe und Lack* (1927), 27; Ch. Moureu and Ch. Dufraisse, *Rev. gen. Caoutchouc*, 4, No. 32, 3; *C.* (1927), II, 984.

<sup>4</sup> *Ber.* 59, 3019 (1926).

# RESIN-FORMING POLYMERIZATION

that of others, the following processes may be used for the purpose—

*Polyoxymethylenes.* Fissional acetylation with acetic anhydride, by which means diacetates containing as many as 22 formaldehyde molecules can be isolated.

Treatment with methyl alcohol and sulphuric acid (H.

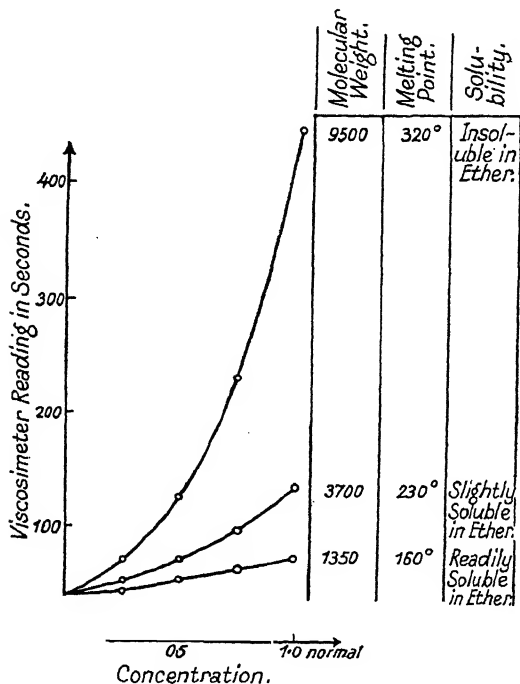


FIG. 3. VISCOSITY OF VARIOUS POLY-ANETHOLS  
(H. Standinger, Ber. 59, 3032 (1926) ).

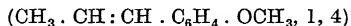
Johner), which results in the production of dimethyl ethers containing as many as 70 formaldehyde molecules.

*Polyindenes.* Hydrogenation (G. Schiemann), by which means paraffin-like substances are obtained which can be heated to 300° C. without decomposing, and the molecular weight of which corresponds to that of the original polymeric substance.



In this manner, complexes containing more than 30 individual molecules have been detected with certainty.

The relationship between molecular weight and viscosity (Berl) is also of importance, and has enabled the union of 20 to 100 individual molecules to be ascertained in the case of polymeric indenenes and anethol:



Regarding the special relationships in the case of anethol, see Fig. 3.<sup>1</sup>

**Colloidal Polymerides.** These substances are of special interest, and are also of exceptional technical importance. It is in no way surprising that with increased molecular weight, substances of more or less decidedly colloidal character should ultimately be obtained. The variation in behaviour is, however, remarkable, and has many puzzling characteristics, even if allowance be made for the influence of the polymerizing agent.

H. Staudinger<sup>2</sup> has attempted to characterize the recognizable types of colloids which are formed, and was thus able to classify them into association colloids, hemicolloids, and eucolloids. These classes of colloids have the following characteristics—

**Association Colloids.** The colloidal particle is not produced by polymerization of individual molecules, but by association of a large number of complexes of a lower order, capable of behaving in this manner. Thus, these are not held together by chemical forces, but by the action of "space-lattice forces"; it is not always possible to decide whether "molecular lattices" with crystal valency lattice forces, or "multipolymeric lattices" with main valency lattice forces, are concerned, as all possible gradations occur. A typical characteristic of association colloids is the possibility of obtaining true solutions of a low degree of molecular dispersion, in so far as the solvent is able to break down the space-lattice attraction, and to form solvates

<sup>1</sup> On the determination of the molecular weight of polymerides by X-ray examination, see J. R. Katz, *Kautschuk*, (1927), 215; *C.* (1927), II, 1206.

<sup>2</sup> *Loc. cit.*

with the liberated molecules or with small molecular complexes. As the powers of the various solvents vary in this respect, complexes of monomolecular, dimolecular, etc., magnitude may be formed, the particular degree of dissociation depending also on the concentration. Should the solvent not possess the power of dissolving the lattice unions, colloidal solutions are formed, the character of which depends on the lyophilic properties of the substances in question. One may assume that in these cases also the original associated complexes are to some degree dissociated, but that the partially dissociated complexes so produced are still very large, relatively to the individual molecules, although even such a partial dissociation enables the solvent to combine, that is, to form solvates. Lyophobic phenomena, therefore, occur only when even partial dissociation is lacking. The colloidal particles are, therefore, by no means always identical with the original poly-complexes.

Another characteristic of association colloids is the circumstance that products of non-colloidal character are obtained by chemical action of a non-dissociating character.

**Hemicolloids.** In hemicolloids the colloid particles are identical with the molecules which are present, but these are not uniform, but are present in mixtures, the constituents of which are molecules of variable, but not exceptionally high, molecular weight. According to H. Staudinger, the mean molecular weight is from 2,000 to 10,000. The solutions usually show a low viscosity, and the viscosity is either uninfluenced or slightly influenced by heating or by the action of reagents. Chemical attack of a non-dissociating character results in products of the same colloidal character. A further distinction from association colloids, which do not form colloidal derivatives, is that in the case of hemicolloids the material properties are dependent on the degree of polymerization.

The solubility, which is always of a colloidal character, is especially high for those solvents which are capable of dissolving the fundamental monomer in a normally disperse manner.

Hemicolloids are always formed under conditions which

ensure the production of mixtures. These conditions are generally fulfilled in polymerization by heating, and more particularly under the influence of catalysts.

**Eucolloids.** In the case of eucolloids, the colloidal particles are also identical with the molecules, but they differ from hemicolloids by the fact that the molecules are uniform in character. Otherwise they have much the same characteristics as hemicolloids, no sharp differentiation from which is possible, as the conception of "uniformity" of molecular weight of the particles is not to be taken literally, but has to be interpreted in a suitable and reasonable manner. It is only possible to prepare eucolloids artificially in exceptional cases, as the methods available for the preparation of polymerization colloids usually result in hemicolloids only, the reason being that complexes of exceptionally high molecular weight are concerned. H. Staudinger estimates the required molecular weight at 50,000 to 100,000, a figure which is attained in nature, but is seldom achievable artificially owing to the strong tendency to exceed the limits of stability. The solid polystyrol, which is obtained in the cold, probably represents an artificial eucolloid of this character, as may be concluded from the fact that polystyrol produced at 100° C. shows an average molecular weight of about 10,000, but yields solutions which are of low viscosity compared to those of the polystyrol produced in the cold.

**Considerations regarding the Practical Production of Resins by Polymerization.** It is naturally of interest to consider the bearing of general experience of the course of polymerization processes on actual resin production.

We may first consider the practical value of the views developed by Herzog and Kreidl (page 43). These views are undoubtedly suitable in a large number of cases for predicting the capacity for polymerization of any particular system, which may then be verified by experiment. It will be clear from the special cases cited (page 103 *et seq.*) that one is not justified in considering the presence of a so-called resinophoric group to be necessarily identical with capacity for the formation of resin. Naturally, the fact must also be taken into account that the practical confirmation of conclusions which are undoubtedly

correct with certain reservations, does not by itself necessarily imply that these can be used for the technical production of resin.

To a certain degree, actual experience of methods of modifying polymerization processes can be utilized. The possibility of altering at will the conditions of the limits of stability of certain higher polymers is of undoubted importance, as is also a recognition of the special action of various agencies on various products, as by suitable combination of several factors it offers the possibility of overcoming the difficulties which are met with in dealing with mixtures of materials capable of polymerization, due to the different behaviour of the individual components.<sup>1</sup> An exact knowledge of the action of the available methods and modifications is particularly important in the manufacture of highly polymerized solid products of hemicolloidal type which are to be used as plastic masses. In these cases, we are not concerned merely with the material as such, but more particularly with its physical condition. The actual mechanical requirements are such that pure polymerization products are usually unsatisfactory. Certain products, such as vitreous styrol, are at first fairly suitable, but lose their characteristics on ageing unless suitable precautions are taken, such as the use of plasticizing agents.

Apart, therefore, from the methods of carrying out the reaction, the means used for ensuring the durability of the elastic properties must be suitably chosen. Those methods used, however, as the result of empirical experiments in individual cases, such as additions of various kinds, are usually only partially suitable, as they frequently are not adapted to the character of the system in question.

Guidance as to the method of procedure in any particular case may be found in the colloid solubility of heavy colloids in such solvents as form a true solution of the polymeric substance. These considerations enable a line of procedure to be adopted by which solid colloidal systems may be produced with some degree of certainty and success, the stability of which is durable, and which are at the same time sufficiently

<sup>1</sup> These considerations apply, for example, to the mixture of cyclopentadiene, styrol, cumarone and indene, used for the manufacture of cumarone resin.

tough, hard, and elastic. Naturally, the choice of plasticizing agents must take into account their volatility under the required conditions of reaction in order that one may be certain that they remain within the system.

In practice, polymerizable materials obtained by special processes and in a practically pure condition are only used occasionally, whilst usually such products are produced as required by a previous condensation, which may be of a resin-forming character.<sup>1</sup> This procedure entails certain advantages together with a number of difficulties which it is difficult to avoid. In a smooth condensation reaction no special difficulties will occur during the subsequent polymerization process, which is usually induced by a combination of heating and catalytic action, as the danger of too far-reaching a solidification of the mass can be avoided by suitable regulation of the temperature, the application of a vacuum, and so on. It is, however, characteristic of a resin-forming combination that it is difficult to carry it to a final point; more particularly, the varying reaction velocities and the various isomers which enter into the reaction or which are formed during its course must be allowed for. Therefore, the course of the polymerization process is often so rapid before the completion of the subsequent condensation that the vaporous by-products, such as water, cannot easily escape from the mass as it increases in viscosity. Special precautions are therefore required in order to avoid the resulting disadvantages, such as the formation of spongy masses or of cracks. It is, therefore, advantageous to use methods which retard polymerization without interfering with condensation. These may consist in the use of anticatalysts, which affect polymerization, and which gradually volatilize, or by the addition of solvents of the right degree of volatility, so that the temperature does not fall below that of condensation. Although it is possible by such means to obtain masses which can be cast and which can then be transformed into solid polymers without bubble formation, the practical operation of the process requires great care and experience. It is, therefore, a particularly important fact that in many cases polymerization

<sup>1</sup> See the chapter on resin-forming condensations (p. 133).

can be carried out under pressure without the formation of bubbles. This process, which is used more particularly in the hardening of phenol-formaldehyde masses (Bakelite C) is of great industrial importance.<sup>1</sup>

The difficulties above indicated are considerably increased if lyophilic colloids are formed, the solvent component of which has to be volatilized. This is, for example, the case in the conversion of urea-formaldehyde products into solid masses of vitreous character, such as Pollopas. These substances, which are produced in aqueous solution, and which are polymerized with great ease, form hydrophilic colloids from which the water can only be removed with difficulty and incompletely on warming. Consequently, all attempts at dehydration naturally result in masses permeated with bubbles. As the addition of alcohol, and so forth, is unsuitable, a solution of the problem was sought and found by scientific research.<sup>2</sup>

The principles of the process, which was found to be satisfactory, consists in liberating the water step by step by syneresis, and after dehydrating sufficiently by this means, in further polymerizing and dehydrating the masses completely in moulds with semi-permeable walls.

The systematic exploitation of the scientific results of resin-forming condensation in technical practice is still in its infancy, but many existing difficulties will undoubtedly be overcome in the future.

<sup>1</sup> Bakelite G.m.b.H., German Pat. 233,803.

<sup>2</sup> F. Pollak and K. Ripper, *Chem. Ztg.*, 48, 569, 582 (1924).

## CHAPTER IX

### RESIN-FORMING POLYMERIZATION

WE have already mentioned (page 52) that polymerization can be considered as a *conditional* function only of certain unsaturated groups. The presence of such groups is, undoubtedly, a necessity for the occurrence of a reaction. The possibility of actually effecting the reaction, however, and the degree of increase of molecular weight which may be attainable depend upon other factors, which are conditioned by the general constitution of the substance, and more particularly by the intensification or weakening of the residual fields, on the saturation of which reaction depends.

Although any system containing a so-called unsaturated group may possibly be capable of polymerization under a suitable stimulus, it must be remembered that the necessary conditions are often of such a character that they are not easily discovered. Moreover, a partial reaction only may occur, and may render the detection of the required result difficult. If, therefore, a substance is described as incapable of polymerization in what follows, it is only to be understood in the sense that the usual agencies are not sufficiently effective to ensure a reasonably smooth reaction. Conversely, when a system is characterized as easily polymerizable, this merely implies that it is sensitive to agencies already known or ordinarily used, with formation of sufficiently stable products. The degree of polymerization which is attained is decided by various circumstances. In any case, slight and far-reaching capacity for polymerization must not be considered as identical.

It is only possible to obtain a clear view of the actual phenomena by considering the varying degrees of reaction obtainable from individual substances, caused by polymerization due to typical polymerizing groups. In this way it is possible also to form a picture of the constitutional factors which activate or weaken the polymerizing tendency.

These considerations are important in the practical application of resin-forming polymerization, as they indicate methods by which a relatively inert system may be induced to become more active. Naturally, we are not concerned merely with the structural characteristics which may be used, but also with the suitable application of the stimulating agencies. The possibilities obtainable by rational combination of these two factors are considerable. Unfortunately, it is for the present scarcely possible to establish definite rules regarding this matter, although certain regularities are well established.

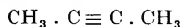
In the following the material is divided into—

1. Substances with unsaturated carbon linkages.
2. Substances with other unsaturated linkages.

### SUBSTANCES WITH UNSATURATED CARBON LINKAGES

**The Acetylene Linkage.** The activity of the group  $\text{—C} \equiv \text{C—}$  is particularly noticeable in the case of acetylene itself. Under the influence of heat (optimum at  $600\text{--}700^\circ\text{C.}$ ) partial polymerization occurs, known as “pyrocondensation,” which leads to the formation of benzene and other aromatic hydrocarbons.<sup>1</sup> These reaction products are fairly resistant to further polymerization. A condensation of acetylene with formation of a substance of high molecular weight occurs<sup>2</sup> under special conditions of reaction, namely, in the presence of certain catalysts, with formation of cuprene<sup>3</sup>, but together with decomposition processes, so that condensations probably occur in this case to an extensive degree. That product of acetylene which shows the most definite resinous character, namely, cuprene, is completely insoluble, and forms light brown masses resembling cork.

In the various alkyl and aryl derivatives of acetylene, the activity of the  $\text{—C} \equiv \text{C—}$  group is comparatively small; thus, for example, dimethyl acetylene



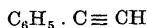
<sup>1</sup> Regarding yields under special conditions, see Chiko Fujio, *C.* (1928), I, 2244.

<sup>2</sup> On combination of acetylene with fats and the formation of plastic masses, see L. G. Bourgoin, U.S. Pat. 1,567,785; *C.* (1926), I, 3293.

<sup>3</sup> See Beilstein, I, 232; Kaufmann, Schneider, *Ber.* 55, 267 (1922).



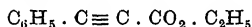
can only be polymerized to hexamethylbenzene by sulphuric acid.<sup>1</sup> Phenylacetylene



is resinified by nitric acid of density 1.35, or by concentrated sulphuric acid.<sup>2</sup> Diphenylacetylene or tolane,

which forms plates or columns of melting point 60° C., distils undecomposed, and is, therefore, extremely stable.<sup>3</sup> Dinaphthylacetylene behaves similarly. Phenyl-naphthylacetylene is described characteristically as having "no strongly unsaturated character."<sup>4</sup>

Even the introduction of the carboxyl group does not increase the reactivity, thus differing from its effect in the case of certain ethylene products. Thus, propiolic acid  $\text{CH} \equiv \text{C} \cdot \text{COOH}$  shows but a very slight tendency to polymerization.<sup>5</sup> The ethyl ester of phenylpropiolic acid,



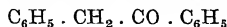
polymerizes on heating for twelve hours at 210° C., practically with the sole formation of 1-phenyl-naphthalene-dicarboxylic acid—2.3—diethylester.<sup>6</sup> Phenylpropiolic acid itself is polymerized by acetic anhydride or phosphorus oxychloride, the action of which results in the quantitative formation of phenyl-naphthalene-dicarboxylic acid or its anhydride.

On the other hand, the strongly activating action of partial substitution by halogens is remarkable and very important. Bromacetylene,  $\text{CH} \equiv \text{CBr}$ , polymerizes to a considerable degree, even by the action of light, with formation of products which are soluble with difficulty and which decompose on melting.<sup>7</sup> Phenylchloracetylene, an oily product, resinifies with

<sup>1</sup> See *Beilstein*, I, 249.

<sup>2</sup> Glaser, *Zts. f. Chem.* (1869), 98; compare *Beilstein*, V, 511.

<sup>3</sup> *Beilstein*, V, 656; with concentrated  $\text{H}_2\text{SO}_4$  desoxybenzoin,



is obtained.

<sup>4</sup> P. Ruggli, M. Reinert, *Helv. chim. Acta*, 9, 67; *C.* (1926), I, 2468.

<sup>5</sup> *Beilstein*, II, 477.

<sup>6</sup> Pfeiffer, Möller, *Ber.*, 40, 3841 (1907); compare *Beilstein*, IX, 634.

<sup>7</sup> Ssabanejew, *Ber.*, 18, Ref. 374 (1885); compare *Beilstein*, I, 245.

polymerization at a fairly high temperature.<sup>1</sup> The corresponding bromo- and iodo-products are polymerized on heating, and also on standing or on illumination. This strongly activating effect of partial halogenation is also to some extent existent in the case of the ethylene linkage, which will be discussed later. On the other hand, fully halogenated acetylenes do not react. Dibromacetylene shows no appreciable capacity for polymerization.<sup>2</sup> Other negative radicals also neutralize the effect produced by partial halogenation; thus, iodo-propionic acid is inert. Analogous results are also obtained on introducing a second carboxyl group, so that the comparatively weak activity of propionic acid vanishes completely in the case of acetylene-dicarboxylic acid.

Thus, the  $\text{—C}\equiv\text{C—}$  group is fairly active in the form of acetylene, and of certain halogen substitution products; but the polymerization products or condensation products, when they attain the complexity necessary for the formation of colloids, are either extraordinarily unstable and even explosive,<sup>3</sup> or form completely insoluble products. It is only by a suitable combination of halogens and alkyl or aryl derivatives that the necessary conditions for the production of products, which could be described as resins, can be obtained. Thus, the products obtained by the *Konsortium für elektrochemische Industrie G.m.b.H.*,<sup>4</sup> by the action of acetylene on suitable organic compounds such as aliphatic, aromatic and alicyclic hydrocarbons, alcohols, glycols, phenols, acids, esters, and so forth, are completely determined in their principal properties by the catalyst which is used. If mercury salts are used, acetaldehyde is first produced by combination with water, and then forms acetaldehyde resin or some aldehyde condensation product by further condensation or reaction with the other organic substances. This reaction must, moreover, be induced by adding

<sup>1</sup> Nef., *Ann.*, 308, 321 (1899); compare *Beilstein*, V, 512.

<sup>2</sup> A. Michael, *J. prakt. Chem.*, 60, 439 (1899).

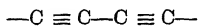
<sup>3</sup> The polymerization of acetylene with formation of highly explosive products takes place, for example, under the influence of the silent electric discharge, by which a high polymeride is formed which decomposes explosively on distillation; see Berthelot, *Compt. rend.* 111, 471 (1890); Losanitsch, *Ber.*, 40, 4659 (1907); *Monatsh.*, 29, 753 (1908), etc.

<sup>4</sup> French Pat. 593,338; Austrian Pat. 103,106; *C.* (1926), II, 1791.

an auxiliary catalyst after saturation of the system with acetylene. If, on the other hand, anhydrous aluminium chloride is used, for example, in dry benzene, a product is obtained which resembles cuprene and can be used as a substitute for cork.

In its behaviour towards the introduction of carboxyl groups, and more particularly of phenyl groups, the acetylene linkage differs typically from the ethylene linkage, although otherwise there are undoubted analogies between the two groups. The ethylene group is not remarkable for exceptional activity, which is rather surprising. Saturation occurs by preference with formation of aromatic complexes, or by addition of water and conversion into aldehydes or ketones.

An accumulation of acetylene groups, particularly when these adjoin one another,



has a strongly activating influence on the power of polymerization. The simplest compound of this character, namely, diacetylene (butadiene),



is a clear liquid of freezing point  $36-37^{\circ}C.$ , which already polymerizes at temperatures of above  $0^{\circ}C.$  The brownish-black products which explode mildly on heating, are infusible at  $350^{\circ}C.$ , and are completely insoluble.<sup>1</sup>

The dimethyl and diethyl derivatives appear to be much more stable, as do also their dihydroxyl derivatives.<sup>2</sup> Diphenyl-diacetylene,



shows no tendency to polymerize, but chars with concentrated sulphuric acid at a gentle heat.<sup>3</sup> On the other hand, di-iododiacetylene<sup>4</sup> and the di-carboxylic acids<sup>5</sup> show a stronger tendency to polymerization.

The circumstance is of great interest, that by the introduction of methylene groups between the two triple linkages it

<sup>1</sup> Fritz. G. Müller, *Helv. chim. Acta*, 8, 826; *C.* (1926), I, 1389.

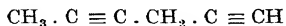
<sup>2</sup> *Beilstein*, I, 266.

<sup>3</sup> Glaser, *Ann.*, 154, 159 (1870).

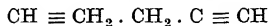
<sup>4</sup> Baeyer, *Ber.*, 18, 2276 (1885); compare *Beilstein*, I, 266.

<sup>5</sup> Baeyer, *Ber.*, 18, 2271 (1885); compare *Beilstein*, II, 810.

appears that a considerably increased activity is obtained, in contrast to the effect of simple methylation at the ends of the chain. Thus, methyl-propargyl-acetylene



is readily polymerizable.<sup>1</sup> Dipropargyl



resinifies on standing in the air and more rapidly on warming, which may possibly be due to oxidation.<sup>2</sup> The influence of the triple linkage is comparable to the action of the ketone group on neighbouring methylene groups.

**The Ethylene Linkage.** The simplest representative of substances with the characteristic linkage  $> \text{C} \equiv \text{C} <$  is ethylene, the tendency to polymerization of which is not so great as that of acetylene, even under the influence of very active stimuli.<sup>3</sup> Thus, it is necessary to work with specially active catalysts, and sometimes under pressure, whereby, according to the latest communications,<sup>4</sup> smooth polymerization is certainly obtained with formation of oily products. Higher olefines, isobutylene, amylene, etc., form dimeric and trimeric polymerides under the influence of boron fluoride, sulphuric acid, zinc chloride, and so forth.<sup>5</sup> But, similarly to acetylene, ethylene, which is substituted by halogen in one carbon atom, shows a far-reaching tendency to polymerize. By the action of light it forms insoluble amorphous masses.<sup>6</sup>

<sup>1</sup> Beilstein, I, 266.

<sup>2</sup> Beilstein I, 266; see also C. C. Coffin and O. Maass, *C.* (1928), I, 1643.

<sup>3</sup> See, *inter alia*, A. R. Olson, C. H. Meyers, *J. Am. Chem. Soc.*, 48, 389; *C.* (1926), I, 2435.

<sup>4</sup> W. Stegemann, *Angew.*, 40, 750 (1927).

<sup>5</sup> J. Houben-H. Meerwein, *Methoden der org. Chem.*, Third Edition (1925), p. 609.

<sup>6</sup> See Beilstein, I, 186, 189, 190; a detailed compilation is given by C. Ellis, *Synthetic Resins and Their Plastics*, pp. 299, *et seq.* On "Polymerization by Light in Solution in the Presence of Catalysts," see German Pat. 362,666; *Kunstst.*, 12, 176 (1922); see also Chem. Fabr. Griesheim-Elektron, German Pat. 281,877 (1913); French Pat. 474,086 (1914); Plotnikow, *Z. wiss. Phot.*, 21, 117 (1922). On the Production of halogenvinylene from Acetylene, etc., see British Pats. 156,117; 156,120-1; U.S. Pats. 1,425,130; 1,436,288. On Films from Vinyl chloride, see L. A. van Dyk, British Pats. 255,837; 260,550; French Pat. 621,604. On Gels, see G. Flumiani, *Kolloid-Zeitschr.*, 45, 152 (1928).

A further reaction is of great interest, namely, that discovered by Matthews and Elder,<sup>1</sup> between ethylene hydrocarbons and sulphur dioxide under the influence of sunlight or of ultra-violet radiation, forming horn-like or glass-like solid masses, the use of which has been proposed as horn and celluloid substitutes. The reaction probably depends on polymerization of a compound of the hydrocarbon with sulphur dioxide.

Cyclic ethylene hydrocarbons, such as cyclohexene, show but a slight tendency to polymerization, which usually only occurs in the presence of especially active catalysts.<sup>2</sup> Cyclo-octene and cyclo-octadiene—1-5, are, on the other hand, fairly reactive, a behaviour assumed to be due to especial stresses in the ring.<sup>3</sup> If halogen atoms are united with the two carbon atoms of the unsaturated linkage in cyclic compounds, these are very active. 1-bromocyclobutene (1),  $C_4H_5Br$ , resinifies on exposure to air.<sup>4</sup> 1,2 dibromocyclobutene (1),  $C_4H_4Br_2$ , is partially converted on standing into a polymeric white powder, insoluble in ether, alcohol, chloroform, and glacial acetic acid.<sup>5</sup>

The phenyl group adjoining the ethylene linkage increases the tendency to polymerize to an exceptional degree.

The most important member of this group is styrol,



which shows an exceptional capacity for polymerization. Styrol boils at  $146^\circ C.$ , and its density is  $0.911$  at  $15^\circ C.$  When exposed to light for three weeks, or heated for three days to  $100^\circ C.$ , or heated for half an hour to  $200^\circ C.$ , this liquid is converted into solid metastyrol ( $C_8H_8$ ) $x$ .<sup>6</sup>

In the dark and at the ordinary temperature, the same change takes place very slowly.<sup>7</sup> On heating a solution of

<sup>1</sup> British Pat. 11,635 (1914); *Kunstst.*, 12, 6 (1912); see also Singer, Kantorowicz, German Pat. 312,917 (1916); *C.* (1919), IV, 375; Singer, French Pat. 515,590; *Kunstst.*, 12, 70 (1922).

<sup>2</sup> W. Stegemann, *loc. cit.*

<sup>3</sup> Willstätter, Waser, *Ber.*, 43, 1180 (1910); Willstätter, Veraguth, *Ber.* 38, 1979 (1905).

<sup>4</sup> Willstätter, v. Schmädell, *Ber.*, 38 1998 (1905).

<sup>5</sup> Willstätter, Bruce, *Ber.*, 40, 3996 (1907).

<sup>6</sup> Blyth, Hofmann, *Ann.*, 53, 314 (1845); Simon, *Ann.*, 31, 267 (1839); Beilstein, V, 475.

<sup>7</sup> Lemoine, *Compt. rend.*, 125, 530 (1897); 129, 719 (1899); compare Beilstein, V, 475.

styrol in toluene in a closed tube to 200° C., meta-styrol is also formed.<sup>1</sup> A polymerizing effect is also produced by concentrated sulphuric acid,<sup>2</sup> sodium-malonic-ester,<sup>3</sup> and similar compounds. According to Krakau,<sup>4</sup> small quantities of bromine, iodine, or sulphur hinder polymerization. The addition of quinone, trinitrobenzene, and so forth, has a similar effect.<sup>5</sup>

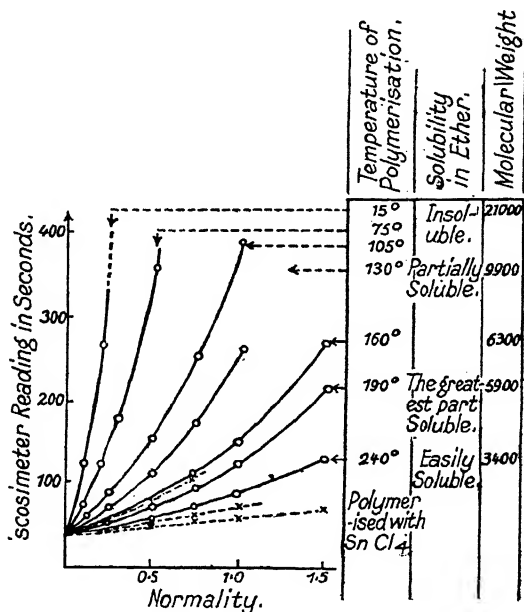


FIG. 4. VISCOSITY OF VARIOUS METASTYROLS  
(Staudinger, Ber. 59, 3031 (1926) ).

Metastyrol ( $d_{13} = 1.054$ )<sup>6</sup> is a white amorphous product which can be powdered. It is insoluble in water and alkalies, very slightly soluble in boiling ether, and inert to bromine and to permanganate. On distilling carefully at about 320° C. it

<sup>1</sup> Berthelot, *Bull. soc. chim.* (2), 6, 294 (1866).

<sup>2</sup> Berthelot, *loc. cit.*, 296.

<sup>3</sup> Vorländer, Hermann. *C.* (1899), I, 730.

<sup>4</sup> Ber., 11, 1261 (1878).

<sup>5</sup> U.S. Pats. 1,550,323-4; *C.* (1926), I, 233.

<sup>6</sup> Scharling, *Ann.*, 97, 186 (1856).

is reconverted into styrol.<sup>1</sup> With styrol and other organic liquids, metastyrol forms colloidal solutions. A mixture of 80 parts of metastyrol with 20 parts of styrol has a vitreous character, and has been recommended as an amber substitute.<sup>2</sup>

Interesting results were obtained during an investigation of the metastyrol obtained under various conditions by M. Brunner and S. Wehrli.<sup>3</sup> According to these investigators, at a low temperature polystyrols are obtained, which melt at a relatively high temperature, are of high molecular weight, and insoluble in ether, and the solutions of which are highly viscous (eucolloids, see page 78); whilst at higher temperatures, or in the presence of catalysts which act in a similar manner, products are obtained of lower melting point, of lower molecular weight, and which are less viscous and more readily soluble. (Hemicolloids, see page 77.) The relationship between these various properties and the molecular weight is indicated comprehensively in Fig. 4 and in the following table of the properties of polystyrol fractions, which were obtained from a polystyrol produced by means of tin tetrachloride, by treatment with solvents.

#### PROPERTIES OF POLYSTYROL FRACTIONS

(Staudinger, *Ber.*, 59, 3032 (1926).)

Properties	Fractions					Unfractionated Mixture
Molecular weight.	1,100	3,000	5,300	7,600	13,000	2,600
Degree of polymerization .	11	29	51	73	125	25
Melting point (°C.)	80-100	111-140	120-150	125-160	135-170	105-150
Viscosity <sup>4</sup> .	60	80	102	129	193	94
Solubility in petroleum ether .	readily soluble	readily soluble	partially soluble	partially soluble	in-soluble	partially soluble

<sup>1</sup> Blyth, Hofmann, *Ann.*, 53, 314 (1945); H. Stobbe and G. Posnjak, *Ann.*, 371, 259 (1909).

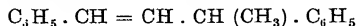
<sup>2</sup> Naugatuck Chem. Co., U.S. Pat. 1,613,674; *C.* (1927), II, 174.

<sup>3</sup> Staudinger, *Ber.*, 59, 3031 (1926).

<sup>4</sup> The figures indicate times of discharge in seconds from an Ostwald viscosimeter. Time of discharge for benzene = 34 seconds.

On the theoretical aspects of the polymerization of styrol, see Kronstein,<sup>1</sup> Stobbe and Posnjak,<sup>2</sup> Stobbe,<sup>3</sup> and others.

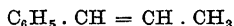
The polymerization of styrol may also be carried out in such a manner that a liquid distyrol<sup>4</sup> is produced of boiling point 310–312° C., and density (at 15° C.) of 1.016.<sup>5</sup>



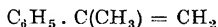
This compound is obtained by heating for several hours at 170° C., with hydrochloric acid of density 1.12,<sup>6</sup> or on standing for some time with a solution of 1 volume of pure sulphuric acid in 9 volumes of glacial acetic acid.<sup>7</sup> With a potassium iodide-iodine solution, a saturated dimeride is obtained,<sup>8</sup> containing a 4-carbon ring. (Formula, page 61.)

Styrols which are substituted by halogens at the ethylene linkage, liberate halogen anhydrides more or less readily with formation of fairly stable acetylene derivatives.

The products obtained on the introduction of alkyl groups into styrol show a rapidly decreasing capacity for polymerization with increasing magnitude of the alkyl group. Propenylbenzene



is converted into a saturated dimeride on boiling with sodium,<sup>9</sup> which can also be obtained by the action of concentrated sulphuric acid. The corresponding product which is methylated in the para-position, namely, 1-methyl-4-propenylbenzene, polymerizes to a thick oil of boiling point-(at 18 mm. pressure), 202–206° C., and density (at 21° C.) of 0.896.<sup>10</sup> Isopropenylbenzene



<sup>1</sup> *Ber.*, 35, 4153 (1902).

<sup>2</sup> *Ann.*, 371, 259 (1909).

<sup>3</sup> *Ann.*, 409, 1 (1914); *Ber.*, 47, 2701 (1914); *Angew.* 35, 578 (1922).

<sup>4</sup> Stobbe Posnjak *loc. cit.* 292, 295.

<sup>5</sup> Fittich, Erdmann, *Ann.*, 216, 187 (1883).

<sup>6</sup> Erlmeyer, *Ann.*, 135, 122 (1865).

<sup>7</sup> Königs, Mai, *Ber.*, 25, 2658 (1892); according to H. Stobbe and G. Posnjak, *Ann.*, 371, 287 (1909), a solid distyrol melting at 124° C., which also shows unsaturated characteristics, is obtained on distilling calcium cinnamate, and is an isomer of the unsaturated dimeride. See also Miller, *Ann.*, 189, 340 (1877); Engler, Leist, *Ber.*, 6, 256 (1873).

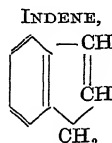
<sup>8</sup> According to H. Stobbe (private communication).

<sup>9</sup> Errera, *Gazz. chim. Ital.*, 14, 509 (1885); *Beilstein*, V, 482.

<sup>10</sup> Klages, *Ber.*, 35, 2253 (1902).



of boiling point 161–162° C., polymerizes on heating with concentrated hydrochloric acid under pressure,<sup>1</sup> or by the action of concentrated sulphuric acid of 66° Be in a freezing mixture,<sup>2</sup> to form a crystalline hydrocarbon  $C_{18}H_{20}$  melting, at 52° C. and boiling at 299–300° C. The product which is methylated in the para-position behaves in a similar manner. Higher homologues appear to be relatively stable.



must also be considered as a styrol derivative, which may be expected to show considerably more activity than propenylbenzene in consequence of the ring formation. Indene is a colourless liquid of boiling point 182.2–182.4° C. at 761 mm. pressure, which solidifies in the cold to form crystals melting at –2° C., and which is very oxidizable. It commences to polymerize at the ordinary temperature and in the dark. On distilling or heating it polymerizes rapidly, para-indene being the main product; whereas by heating for 20 hours under reflux, indene is converted into para-indene to the extent of 30 per cent only. The process is accompanied by fission processes which lead to the formation of hydrindene and truxene. ( $C_{27}H_{18}$ .)<sup>3</sup> Indene is contained in the same coal-tar fraction as cumarone, from which it cannot be separated in a simple and practical manner. The so-called cumarone resin is a mixture of polymers of indene and cumarone, which is obtained technically on a very large scale by the action of concentrated sulphuric acid, aluminium chloride, and so forth,<sup>4</sup> on these substances or on the corresponding concentrated tar fractions.

A para-indene which was obtained by the action of sulphuric acid formed a white mass soluble in benzene, of melting point

<sup>1</sup> Grignard, *C.* (1901), II, 624; *Beilstein*, V, 490.

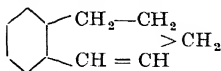
<sup>2</sup> Tiffeneau, *Ann. chim.*, (8), 10, 158 (1907).

<sup>3</sup> Weger, Billmann, *Ber.*, 36, 640 (1903); *Beilstein*, V, 515.

<sup>4</sup> Kraemer, Spilker, *Ber.*, 33, 2260 (1900); compare *Ber.*, 23, 3278 (1890).

210° C.;<sup>1</sup> this melting point varied slightly in consequence of the presence of varying proportions of cumarone and methylcumarone.<sup>2</sup> By varying the quantity and concentration of the sulphuric acid, Marcusson<sup>3</sup> obtained various para-indenes. Thus, with concentrated sulphuric acid a product was obtained which was insoluble in ether and melted at 210° C. On the other hand, with dilute acid or with very small amounts of concentrated acid, a mixture was obtained of a substance, melting at 165° C., soluble in ether, and insoluble in ether-alcohol. Para-indene distils at 290–340° C. with formation of indene, hydrindene<sup>4</sup> and truxene.<sup>5</sup> On the theory of the polymerization of indene, see H. Staudinger.<sup>6</sup> H. Stobbe and E. Farber<sup>7</sup> carried out an exceptionally complete series of experiments on the polymerization of indene under the influence of the various agencies, such as heat, pressure, light, sulphuric acid and various salts. Among the products they also obtained one which they characterized as meta-indene. Very complete investigations have been made by G. S. Whitby and Morris Katz<sup>8</sup> on the variations of the properties of the indene polymers obtained by the action of heat, antimony-pentachloride and tin chloride. On a resin suitable for varnishes obtained by the catalytic hydrogenation of poly-indene, see H. Staudinger.<sup>9</sup>

The methylindenes, such as 1-methylindene, boiling point 205–206° C.,<sup>10</sup> and a mixture of isomeric methylindenes obtained from the coal-tar fraction of 200–210° C. after removal of the bases and tar acids,<sup>11</sup> also show a capacity for polymerization. They are also characterized by being easily oxidized. In the case of cyclic homologues, such as phenocycloheptene,



<sup>1</sup> Kraemer, Spilker, *Ber.*, 33, 2260 (1900).

<sup>2</sup> Kraemer, Spilker, *Ber.*, 34, 1887 (1901).

<sup>3</sup> Gläser, *Brenn. Chem.* (1921), 113.

<sup>4</sup> Kraemer, Spilker, *Ber.*, 33, 3016 (1900).

<sup>5</sup> Weger, *Angew.*, 22, 345 (1900).

<sup>6</sup> *Ber.*, 59, 3032 (1926).

<sup>7</sup> *Ber.*, 57, 1838 (1924).

<sup>8</sup> *J. Amer. Chem. Soc.*, 50, 1160; *C.* (1928) I 2821

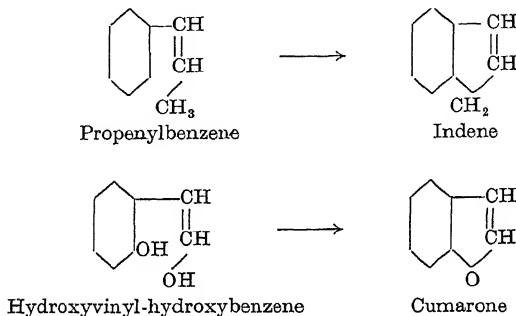
<sup>9</sup> Swiss Pat. 121,817; *C.* (1928), I, 2465.

<sup>10</sup> Roser, *Ann.*, 247, 159 (1888).

<sup>11</sup> Boes, *Ber.*, 35, 1762 (1902).

the presence of the capacity of polymerization is very doubtful.<sup>1</sup>

Indene may be considered as a propenylbenzene modified by ring formation, and is closely allied to cumarone, which must be considered as a cyclic ether of a hydroxyvinyl-1-hydroxybenzene-2.



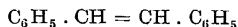
Cumarone,  $C_8H_6O$ , was obtained by Kraemer and Spilker<sup>2</sup> from those constituents of light tar oils boiling at 168–175° C. after removal of the phenols and bases. It forms a clear liquid of peculiar smell, of specific gravity 1.096, and boils at 168.5–169° C. (Fittig and Ebert), or at 172° C. according to Weger. Pure cumarone shows a distinct tendency to polymerize to a limited degree, which generally leads to the formation of tetramerides, in presence of aluminium-chloride, strong alkalies and strong mineral acids.<sup>3</sup> The product of this polymerization is known as para-cumarone, and forms a hard, brittle mass of conchoidal fracture, of specific gravity 1.25 at 19° C., melting point 107–108° C., which is soluble in benzene. It should be noted that the polymerization can be carried further, with formation of insoluble products, for example, by the action of an excess of 95 per cent sulphuric acid. Regarding the technical importance of the polymerization of cumarone, see the chapter on Cumarone Resins.

<sup>1</sup> Kipping, Hunter, *J. Chem. Soc.*, 83, 247 (1903).

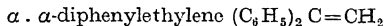
<sup>2</sup> *Ber.*, 23, 98 (1890).

<sup>3</sup> Kraemer, Spilker, *Ber.*, 33, 2257 (1900).

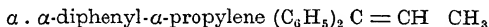
The tendency to polymerization of styrol is remarkably reduced by substitution by aryl groups; thus, iso-stilbene (cis-stilbene) is readily converted into stilbene (cis-trans-form) on heating to about 170–178° C., also by sunlight or in presence of traces of bromine or iodine.<sup>1</sup> All that occurs, therefore, is a saturation of valencies within the molecule. Stilbene itself,



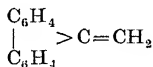
forms a crystalline dimolecular stilbene of freezing point 163° C. by the action of light for a considerable period in benzene solution.<sup>2</sup> By the continued action of ultra-violet radiation it is partially converted into iso-stilbene.<sup>3</sup> This insensitive behaviour contrasts to a certain degree with its power of autoxidation, by which means it easily forms benzoic acid and resinous products. In the case of unsymmetrically substituted products, the reduction of the sensitiveness is still more marked; thus whilst



is capable of conversion into a dimeride,<sup>4</sup>



hardly shows any further power of polymerization.<sup>5</sup> On the other hand, diphenylethylene



forms a polymer of high molecular weight with extraordinary ease even in diffuse light, and more slowly in solution.<sup>6</sup>

<sup>1</sup> Compare *Beilstein* V, 633.

<sup>2</sup> Ciamician, Silber, *Ber.*, 35, 4129 (1902); *Gazz. chim. Ital.*, 34, II, 143. The nature of the solvent plays an important part; thus, for example, solutions in alcohol, ether, chloroform, trichlorethylene and pyridine are inert. The photo-equilibrium inclines in the direction of the dimeride in light of long wave-length, and in that of the monomeride in light of short wave-length. See also H. Stobbe, *Ber.*, 47, 2703 (1914); *Angew.*, 35, 587 (1922).

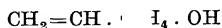
<sup>3</sup> Stoermer, *Ber.*, 42, 4871 (1909).

<sup>4</sup> Hildebrand, *Dissertation*, Strassburg (1909); Lebedew, Andreewsky, Matyuschkina *Ber.* 56, 2349 (1923).

<sup>5</sup> See, however, Hepp, *Ber.*, 7, 1412 (1874).

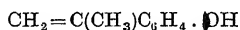
<sup>6</sup> Wieland, Reindel, Ferrer, *Ber.*, 55, 3313 (1922).

The hydroxyphenyl group induces a considerable increase of sensitiveness; thus, o-hydroxystyrol

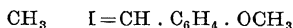


polymerizes on storage, on exposure to light, and particularly on heating on a water bath, to a dimeride in the form of a solid mass insoluble in alkalies and as hard as glass.<sup>1</sup> The formation of polymerides of still higher molecular weight can be deduced from the fact that a bright red resin is produced with concentrated sulphuric acid. No observations appear to have been made on m-hydroxystyrol.<sup>2</sup> The corresponding para-derivative is unknown.<sup>3</sup> The relationships regarding the methoxyl derivates are better known. Thus, o-methoxy-styrol polymerizes to a hard product on storage,<sup>4</sup> under the influence of sunlight,<sup>5</sup> on heating to 150° C.,<sup>6</sup> and by the action of acids;<sup>7</sup> m-methoxyl-styrol is converted in a few days by direct sunlight into a transparent brittle mass;<sup>8</sup> p-methoxystyrol (p-vinyl-anisol) polymerizes spontaneously to form a polymer of high molecular weight.<sup>9</sup> The conclusion may be drawn that substitution in the para-position is particularly effective.

Methylated products are also sensitive; thus, o-isopropenylphenol,



polymerizes readily on standing.<sup>10</sup> Anethol, p-methoxypropenyl-benzene,



is converted into anisoin by small quantities of concentrated

<sup>1</sup> Fries, Fickewirth, *Ber.*, 41, 370 (1908).

<sup>2</sup> G. Komppa, *Dissertation*, Helsingfors; *Ber.*, 27 R., 677 (1893).

<sup>3</sup> Compare *Beilstein*, VI, 561.

<sup>4</sup> Pschorr, Einbeck, *Ber.*, 38, 2076 (1905).

<sup>5</sup> Klages, *Ber.*, 36, 3587, Footnote 2 (1903).

<sup>6</sup> Perkin, *J. Chem. Soc.*, 33, 212 (1878).

<sup>7</sup> Pschorr, Einbeck, *loc. cit.*

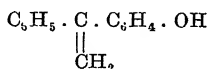
<sup>8</sup> *Loc. cit.*

<sup>9</sup> Tiffeneau, *Ann. chim.*, (8), 10, 349 (1907); compare *Beilstein*, VI, 561; H. Stobbe, K. Toepfer, *Ber.*, 57, 484 (1924).

<sup>10</sup> Hoering, Braun, *C.* (1909), I, 1522.

sulphuric or phosphoric acid,<sup>1</sup> indicating preliminary fission with formation of anisaldehyde. On treating with tin tetrachloride, however, higher polymers of the hemicolloid type are produced. (See page 77.) On the capacity for polymerization of the kindred eugenol and safrol derivatives, see Ciamician and Silber.<sup>2</sup>

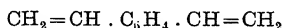
Nothing definite is known regarding the behaviour of diaryl-substituted products. At any rate, no noticeable tendency to polymerization is shown, for example, by  $\alpha$ -phenyl- $\alpha$ -hydroxyphenyl-ethylene,<sup>3</sup>



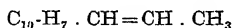
or by the dimethylether of  $\alpha, \alpha$ -Bis-(4 hydroxyphenyl)-ethylene,<sup>4</sup>



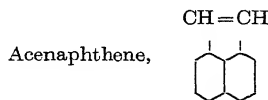
Regarding other aryl substituted ethylenes, we may mention that 1-4-divinylbenzene



resinifies completely on heating or on attempting to distil it.<sup>5</sup> Regarding vinyl-naphthalenes, it is stated that 1-propenyl-naphthalene,



polymerizes partially on boiling.<sup>6</sup>



<sup>1</sup> Cahours, *Ann.*, **41**, 63 (1842); on poly-anethols compare Staudinger, *Ber.*, **59**, 3032 (1926).

<sup>2</sup> *Ber.*, **42**, 1389 (1909); see also C. Ellis, *Synth. Resins and Their Plastics*, p. 304.

<sup>3</sup> Stoermer, Kippe, *Ber.*, **36**, 4003 (1903); **37**, 4166 (1904); *Ann.*, **342**, 4 (1905).

<sup>4</sup> Gattermann, *Ber.*, **22**, 1132 (1889).

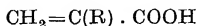
<sup>5</sup> Ingle, *Ber.*, **27**, 2528 (1894).

<sup>6</sup> Tiffeneau, Daudel, *Compt. rend.*, **147**, 679 (1908); compare *Beilstein*, V, 598

is stable.<sup>1</sup> Anthracene, which may be considered as a kindred substance, can, as is well known, be converted into crystalline dianthracene.

### **Influence of the Carboxyl Group on the Ethylene Linkage.**

The carboxyl group exercises a polymerizing tendency on the ethylene linkage in those cases only in which it occurs in an adjoining position, and when, in addition, the ethylene group is placed at the end of the chain, so that the following structure exists—



This circumstance reminds one of the peculiarity of the methylene ketones. (See page 105.) The acids in question show quite considerable power of polymerization, particularly in the form of their esters.

The simplest representative of this group is acrylic acid,



a liquid with a penetrating smell of acetic acid, of freezing point 13° C. and boiling point about 139° C. which polymerizes on boiling.<sup>2</sup> The methyl ester is much more reactive, as it is converted into a solid polymer on standing for some time, on heating and on exposure to sunlight.

This polymer is a transparent jelly which cannot be melted without decomposition and cannot be distilled at ordinary pressure. It is almost without odour, has a density of 1.2222 at 18.2° C., is insoluble in acids, alkalies, water, alcohol and ether, and swells to a slight extent in boiling glacial acetic acid or benzene without dissolving. If this solid substance is distilled at 115 mm. pressure, a liquid polymeric modification distils which is insoluble in water, but easily soluble in alcohol and ether.<sup>3</sup>

The ethyl ester of acrylic acid polymerizes on distillation.<sup>4</sup>

<sup>1</sup> Compare *Beilstein*, V, 625.

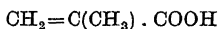
<sup>2</sup> Rüber, Schetelig, *Ztschr. phys. Chem.*, 48, 348 (1904); *J. prakt. Chem.* (2), 61, 494 (1900); compare *Beilstein*, II, 398.

<sup>3</sup> Kahlbaum, *Ber.*, 13, 2348 (1880); 18, 2108 (1885). Compare *Beilstein*, II, 399.

<sup>4</sup> Weger, *Ann.*, 221, 80 (1883); van der Burg, *Rec. trav. Chim.*, 41, 21 (1922).

The polymerides of the ester were proposed as rubber substitutes,<sup>1</sup> and as resinous vehicles for pigments, and so forth.

O. Röhm<sup>2</sup> produces polymerides by exposure of the liquid esters, for example, the allyl-alcohol ester, to light. These polymerides can be used as varnishes or vehicles for pigments after solution in acetone, the esters of the lower fatty acids and other solvents; it is stated that in this way coatings are produced which are "quite inert to weathering and many other chemical influences, colourless, transparent, elastic and very tough." *Methylacrylic acid*,



is converted quantitatively into a polymeride on prolonged heating in a sealed tube to 130° C.,<sup>3</sup> or on prolonged storage at the ordinary temperature, and more quickly on the addition of a few drops of hydrochloric acid.<sup>4</sup> The polymeric methacrylic acid forms a porcelain-like mass which can be obtained as a light flocculent powder by solution in absolute alcohol and precipitation with anhydrous ether. It is fairly easily soluble in alcohol, more slowly in water with preliminary gelatinization, soluble with difficulty in phenol, very slightly soluble in acetone and insoluble in chloroform, benzene or glacial acetic acid. Its molecular weight was found by Mjöen<sup>5</sup> to correspond to  $(\text{C}_4\text{H}_6\text{O}_2)_8$ . The product becomes yellowish in colour at 150° C., shows signs of decomposition at about 200° C., and volatilizes at 300° C. without melting. It is scarcely attacked by fuming nitric acid, chromic acid, molten potash or concentrated sulphuric acid, but is dissolved slowly but completely by ammonia.

<sup>1</sup> German Pat. 262,707 (1912); British Pat. 613 (1913); Belgian Pat. 252,531. Compare *Kunstst.*, 3, 276, 315, 375 (1913).

<sup>2</sup> German Pat. 295,340 (1915); Swiss Pat. 79,804; Austrian Pat. 79, 326. Compare *Kunstst.*, 7, 24, 305 (1917); 9, 261 (1919); 10, 215 (1920); *C.* (1917), I, 42.

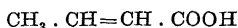
<sup>3</sup> Fittig, *Engelhorn, Ann.*, 200, 71 (1880); Mjöen, *Ber.*, 30, 1228 (1897).

<sup>4</sup> Bischoff, *Walden, Ann.*, 279, 110 (1894). Compare *Beilstein*, II, 422.

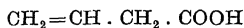
<sup>5</sup> *Loc. cit.*



Neither the isomeric acids nor the homologous products show any tendency to polymerize. Thus, the crotonic acids



vinyl-acetic acid,



and even  $\gamma$ -bromo-vinylacetic acid,



are not polymerizable.

Whilst free itaconic acid



shows a tendency to be converted into its anhydride or into isomers, its esters (the dimethyl, diethyl, and diamyl esters) have a strong tendency to polymerization with formation of vitreous masses.<sup>2</sup>

Even when the ethylene linkage is present in cyclic products, a neighbouring carboxyl group induces no tendency to polymerization.<sup>3</sup> The corresponding esters are also stable.

In the simultaneous presence of the phenyl and carboxyl groups, each of which are powerful promoters of polymerization, an exceptional reactivity of the ethylene linkage might be expected, but this is by no means the case; on the contrary, the products show but little tendency to polymerize; thus, these individually active influences largely neutralize each other. For example, *cinnamic acid* exists in the form of various isomers in which a varying degree of saturation probably occurs within the molecule, but polymerizes merely to crystalline dimeric products, namely, truxillic and truxinic acids.<sup>4</sup> Further, styrol is easily formed on heating, with

<sup>1</sup> It is prepared from the corresponding nitrile by treatment with fuming hydrochloric acid. See Lespieau, *Ann. chim.* (7), 11, 274 (1897).

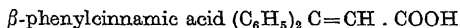
<sup>2</sup> See Knops, *Ann.*, 248, 176, 201 (1888); Anschütz, *Ber.*, 38, 693 (1905); 14, 2787 (1881); Fittich, Boek, *Ann.*, 331, 174 (1904); Walden, *Ztschr. phys. Chem.*, 20, 382 (1896); compare *Beilstein*, II, 762.

<sup>3</sup> See *Beilstein*, IV, 41, *et seq.* This is true, for example, for cyclohexene and cyclopentene carboxylic acids, and also for cyclopentene-acetic-acids, etc., and for their esters.

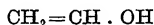
<sup>4</sup> See especially H. Stobbe, Alice Lehfeldt, *Ber.*, 58, 2415 (1925), regarding the action of light of various wave-lengths.

separation of carbon dioxide. The esters are more sensitive. Thus, the ethyl ester of cinnamic acid polymerizes on very long storage in the dark to form a white insoluble powder which is depolymerized on heating with potash.<sup>1</sup>

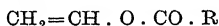
On substituting acrylic acid by more than one phenyl group, exceptionally stable products are obtained, some of which distil undecomposed in spite of their high melting points; for example,



Having dealt with the above group of substances, in which the carboxyl group is directly attached to the unsaturated carbon atoms, we must now consider a further group in which it is attached by ester formation, that is, by means of an oxygen atom. Such products are represented by the so-called vinyl esters<sup>2</sup> which are derived from vinyl alcohol,



a desmotropic form of acetaldehyde, which is not stable in the free state. These products, therefore, contain the exceptionally sensitive grouping,



which is very similar to that of the acrylic acid esters, as in this case also the sensitiveness is due to the presence of the vinyl group.

Polymerides of the vinyl esters have been recommended for the manufacture of plastic masses and artificial resins under the name of "Mowilith" products.<sup>3</sup> Polymerization is induced

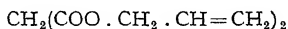
<sup>1</sup> Kronstein, *Ber.*, 35, 4152 (1902); compare *Beilstein*, IX, 582; on resin formation in the case of allyl-cinnamic acid esters, by very prolonged heating to very high temperatures, see C. Ellis, *Synth. Resins*, p. 305; regarding the methyl ester, see H. Stobbe, *Ber.*, 58, 2859 (1925), where reference to further literature will be found.

<sup>2</sup> On their production from acetylene and carboxylic acids see Chem. Fabr. Griesheim-Elektron, German Pat. 271,381 (1912).

<sup>3</sup> Chem. Fabr. Griesheim-Elektron, German Pats. 281,687-S (1913); 290,544 (1913); 291,299 (1915); British Pat. 15,271 (1914); French Pat. 474,086 (1914); Swiss Pat. 71,809; compare *Kunstst.*, 5, 32 (1915); 6, 97, 135, 263 (1916); 11, 10, 119 (1921); 12, 151 (1922); regarding the degree of polymerization, see H. Staudinger, K. Frey, and W. Starek, *Ber.*, 60, 1782 (1927).

by the action of light, by heating, and so forth, and is considerably accelerated by the addition of oxidizing agents, such as superoxides, ozonides and organic acid anhydrides in conjunction with materials which liberate oxygen, such as perborates and percarbonates, and metallic oxides such as silver oxide.<sup>1</sup> As raw materials, the vinyl esters of acetic acid and of chloracetic acid are especially mentioned. The solvents used for the formation of varnishes are ethyl esters, ketones, nitrohydrocarbons or aldehydes, to which other solvents, diluents, or gelatinizing agents may be added in the interests of economy, such as petroleum ether, benzene, chlorobenzene, and so forth.<sup>2</sup> Latterly, however, products have been successfully obtained which are soluble in the most ordinary and cheapest varnish solvents, such as alcohol, benzene, and so forth.<sup>3</sup> If polymerized vinyl acetate is saponified<sup>4</sup> one obtains polyvinyl alcohol.<sup>5</sup> This substance, as also its derivatives, are converted by treatment with sulphur or sulphur chloride, to which accelerators such as piperidine may be added, into masses resembling india-rubber.<sup>6</sup>

A moderate degree of polymerizing capacity is shown by allyl malonate,



which thickens to form a balsam on heating for 24 hours to 170° C., in a closed tube.<sup>7</sup>

<sup>1</sup> German Pat. 281,688 (1913); *Kunstst.*, 5, 32 (1915); compare 11, 10 (1921).

<sup>2</sup> See Consortium f. elektrochem. Ind., British Pat. 261,748; *C.* (1927), I, 1892; German Pat. 451,692, on the production of an indiarubber-like mass upon heating polymerized vinyl alcohols or their derivatives, such as their esters, ethers, acetals or homologues, with sulphur or sulphur halides, such as sulphur-monochloride, to which various accelerators, such as pyridine, may also be added.

<sup>3</sup> See Consortium f. elektrochem. Ind., German Pat. 446,562 (1926); *C.* (1927), II, 1100; see also I. G. Farbenind., German Pat. 449,115; British Pat. 280,246 (Heating vinyl esters with aliphatic aldehydes).

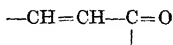
<sup>4</sup> On polymeric vinylacetate, see H. Staudinger, K. Frey, W. Starck, *Ber.*, 60, 1782 (1927).

<sup>5</sup> On polyvinyl alcohol, see also W. O. Herrmann and W. Haehnel, *Ber.*, 60, 1658 (1927).

<sup>6</sup> Consortium f. elektrochem. Ind., British Pat. 261,748; *C.* (1927), I, 1892.

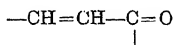
<sup>7</sup> Kronstein, U.S. Pat. 843,401 (1907); see C. Ellis, *Synthetic Resins and their Plastics*, p. 305.

**Influence of the Carbonyl Group on the Ethylene Linkage.**  
The combination of carbonyl with the ethylene linkage in an adjoining position leads to the grouping



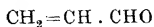
which is regarded by W. Herzog and J. Kreidl<sup>1</sup> as a resinophoric group.

As is evident from what we have mentioned on page 63, the carbonyl group itself must be considered as a complex capable of polymerization. It is, therefore, natural that the above-mentioned resinophoric combination should show special sensitiveness, as two centres of activity are present which might be expected to reinforce each other. It is, however, found that in the first instance this increased reactivity is confined to the ethylene group; in other words, the carbonyl group plays a similar part with regard to the ethylene group to any other negative substitute, such as halogen or phenyl. But, just as the presence of several halogen atoms or aryl groups results in a reduced reactivity, so the addition of negative substitutes to the combination



results in no increased tendency to polymerize, but to a definite weakening. This fact is demonstrated by the following summary:—

The simplest combination of ethylene and carbonyl is present in *acrolein*,



which is a clear, highly refractory liquid of penetrating smell, with an intense action on the eyes and mucous membranes, boiling at 52.4° C.<sup>2</sup>

Acrolein has exceptional powers of polymerization, and is easily converted on standing into an amorphous white

<sup>1</sup> *Angew.*, 35, 465, 641 (1922); 36, 471 (1923).

<sup>2</sup> See *Beilstein*, I, 726.

substance known as disacryl,<sup>1</sup> which is insoluble in water, alcohol, acids, and alkalis.<sup>2</sup> On heating acrolein with 2 to 4 volumes of water to 100° C. for 8 days, a resin is formed which commences to melt at 60° C. and evolves acrolein at 100° C.<sup>3</sup> It is somewhat soluble in water and easily soluble in alcohol or ether, which may, perhaps, be due to a slight formation of hydroxy-compounds. Acrolein forms with alcoholic potash the potassium salt of hexacrolic acid ( $C_3H_4O$ )<sub>6</sub>, which is a yellow amorphous substance, insoluble in water, but easily soluble in alkalis, alcohol or ether.<sup>4</sup> The influence of light and heat on the polymerization of acrolein was investigated by Moureu, Murat and Tampier.<sup>5</sup>

Small quantities of the carbonates or hydroxides of the alkalis accelerate very considerably the polymerization of acrolein when dissolved in water.<sup>6</sup> The following further accelerators of the reaction are mentioned by C. Moureu and C. Dufraisse:<sup>7</sup> quick-lime, lead hydroxide, ammonia, methylamine, aniline, ferric chloride and lead acetate. Free mineral acids are unsuitable. Products of varying solubility are produced according to the duration of the reaction. By prolonged reaction, McLeod and Nef obtained products insoluble in hot water, carbon disulphide, benzene, ether, petroleum ether and glacial acetic acid, but soluble in warm 95 per cent alcohol, the alcoholic solution of which, when heated for a short time to 100° C., separated a substance completely insoluble in organic solvents which did not melt at 180° C. According to Moureu and Dufraisse, with a shorter reaction period a substance is obtained which is insoluble in water and in hydrocarbons, readily soluble in the cold in many organic solvents, such as alcohols, ketones and organic acids, and which may

<sup>1</sup> By the addition of small amounts of phenols, the formation of disacryl can be prevented for a long period; see Moureu, Dufraisse, German Pat. 340,871 (1920); *Kunstst.*, 12, 28 (1922).

<sup>2</sup> Redtenbacher, *Ann.*, 47, 141 (1843).

<sup>3</sup> Geuther, Cartmell, *Ann.*, 112, 10 (1859).

<sup>4</sup> Claus, *Ann. Spl.*, 2, 120 (1862-3); compare Beilstein, *loc. cit.* 727.

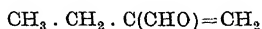
<sup>5</sup> *Ann. chim.*, 15, 221 (1921); *Compt. rend.*, 172, 1267 (1921).

<sup>6</sup> Nef, *Ann.*, 335, 220 (1904); McLeod, *Am. Chem. J.*, 37, 34 (1907); compare Beilstein, I, 726.

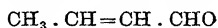
<sup>7</sup> British Pat. 141,058 (1920); *Kunstst.*, 10, 183 (1920); German Pat. 349,188; *C.* (1922), II, 880; French Pat. 509,620; *Kunstst.*, 12, 55 (1922).

be used for the production of varnishes. These various resins showing varying degrees of solubility, softened at about 80–120° C., and decomposed on further heating with the evolution of a strong odour of acrolein. Decomposition also occurs on heating with dilute acids and caustic alkalis.

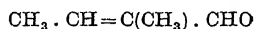
$\alpha$ -ethyl-acrolein,



apparently also polymerizes very easily.<sup>1</sup> Crotonic aldehyde,



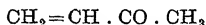
also shows a tendency to polymerize. On the other hand, tiglic aldehyde,



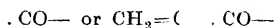
may be described as non-polymerizable. In the case of other unsaturated aldehydes, also, no polymerization phenomena have been observed. Even cinnamic aldehyde,

is but very slightly polymerizable.<sup>2</sup>

Ketones corresponding to acrolein and analogous aldehydes, such as vinyl-ketones, show reactivity; thus, methylvinyl-ketone,



polymerizes easily,<sup>3</sup> as do also ethylvinyl-ketone<sup>4</sup> propylvinyl-ketone,<sup>5</sup> and similar compounds.<sup>6</sup> Other aliphatic ketones, which do not show the above characteristic structure,



<sup>1</sup> Compare *Beilstein*, I, 733.

<sup>2</sup> Compare Stobbe, *Ber.*, 58, 2861 (1925). On the apparently more reactive furfuracrolein,  $\text{C}_4\text{H}_5\text{O} \cdot \text{CH}=\text{CH} \cdot \text{CHO}$ , see W. König, *Ber.*, 58, 2564 (1925).

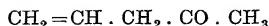
<sup>3</sup> Blaise, Maire, *Compt. rend.*, 142, 217 (1906); Maire, *Bull. Soc. chim.*, (4), 3, 277, 278 (1908); compare *Beilstein*, I, 728.

<sup>4</sup> Blaise, Maire, *loc. cit.*; compare *Beilstein*, I, 732.

<sup>5</sup> *Loc. cit.*; compare *Beilstein*, I, 734.

<sup>6</sup> Farbenfabr. F. Bayer & Co., German Pat. 309,224 (1917); capacity of polymerization of the so-called methylene-ketones, to form colourless, hard, elastic masses. See *Kunstst.*, 10, 149 (1920). On the polymerization of ethoxy-methylene-diacetyl,  $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}=\text{CH} \cdot \text{O} \cdot \text{C}_2\text{H}_5$ , see O. Diels, J. Petersen, *Ber.*, 55, 3452 (1922).

show no capacity for polymerization. This is true, for example, of vinylacetone,



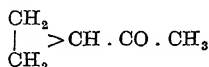
ethylidene-acetone,



and mesityloxide,

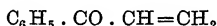


It should be noted that the trimethylene ring renders a carbonyl group capable of polymerization, as is shown by the behaviour of methylocyclopropyl-ketone,

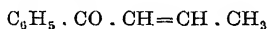


which readily polymerizes, particularly in the presence of acids.<sup>1</sup>

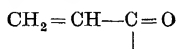
Vinylphenylketone,



may be mentioned as an instance of an aromatic compound containing the above-mentioned reactive atomic group. It is an oil which gradually changes in the light into a product of a horn-like character.<sup>2</sup> The product which is methylated in the methylene group, namely,



shows no such behaviour.<sup>3</sup> From these examples it is clear that the presence of the group,



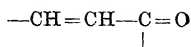
induces a decided tendency to polymerization, so that even mild agencies effect the transformation of substances contained in this group into polymerides of high molecular weight and of an infusible character. It is also clear that when this group

<sup>1</sup> Perkin, *Ber.*, 17, 1441 (1884); *J. Chem. Soc.*, 47, 835 (1885); see *Beilstein*, VII, 8.

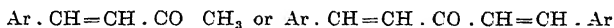
<sup>2</sup> Schäfer, Tollens, *Ber.*, 39, 2187 (1906).

<sup>3</sup> See *Beilstein*, VII, 368.

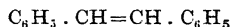
is modified, the reactivity is very considerably reduced and may be practically absent. With regard to the compounds investigated by W. Herzog and J. Kreidl,<sup>1</sup> from the resin-forming character of which a resinophoric character of the grouping



was deduced, it must be stated that these certainly cannot be counted amongst specially reactive substances. The substances with which they experimented were almost entirely confined to aryl-olefine and diaryl-diolefine ketones of the general formulae,



which were obtained by condensation of aromatic aldehydes with acetone. In accordance with the behaviour of the phenyl-ethylenes, such as stilbene,



none of these olefine ketones can be expected to form higher polymers than dimerides in most cases. In agreement with this view, the transformation products which were obtained were all soluble and fusible. In many cases it is questionable whether polymerization occurred at all. This can be concluded from the circumstance, for example, that the resin from dibenzylidene acetone formed a tetrabromide of the monomeride by a smooth reaction.<sup>2</sup> This tetrabromide could be obtained without difficulty in crystalline form, melting at 207–208° C. It is, of course, possible that the bromine exercised a deep depolymerizing effect, but even this would be merely a confirmation of the presence of loose complexes such as associations.

The resinous character of the transformation products is, moreover, in no way surprising. Apart from the fact that the formation of isomers is to be expected, the possibility and considerable probability of a partial decomposition of these substances, which are all very oxidizable, must be taken into

<sup>1</sup> *Angew.*, 35, 465, 641 (1922); 36, 471 (1923); *Chem. Ztg.*, 49, 119 (1925); German Pat. 397,603; *C.* (1924), II, 1412.

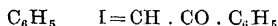
<sup>2</sup> *Angew.*, 35, 466–7 (1922).



account. Although Herzog and Kreidl carried out the various polymerizations in a stream of carbon-dioxide, the periods of heating were very long, amounting to several hours. Moreover, it is very difficult to exclude oxygen absolutely. In any case, considerable possibilities for the occurrence of by-reactions were present, and even if these occurred to a relatively small extent, they would be sufficient to nullify the crystallizing tendency of the polymerides which were formed, and thus to produce a resinoid condition and to stabilize it to a sufficient degree.

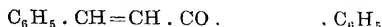
These circumstances must be taken into account, as otherwise false conclusions might be drawn. The accumulation of groups which are in themselves reactive in no way causes a corresponding increase of the capacity for polymerization, which may even become extremely small.<sup>1</sup> Such an accumulation of reacting groups merely offers opportunity for the occurrence of by-reactions, which may form the necessary quantity of impurity in the actual transformation product to confer on this the resinoid condition. It must also be remembered that the formation of the typical mixture is mainly due to the partial transformation of the raw material, and is, therefore, a mixture of monomerides and dimerides.

Regarding the individual behaviour of the products investigated by W. Herzog and J. Kreidl, it may be mentioned that according to H. Wieland,<sup>2</sup> benzalacetophenone,



may be converted, by the influence of dilute sulphuric acid in acetic anhydride solution, into a crystalline dimeride of melting point 134° C. Moreover, the following products could be converted into "resins" by heating for several hours in an atmosphere of carbon-dioxide—

*Dibenzylidene-acetone,*

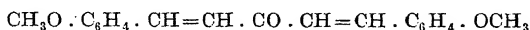


<sup>1</sup> For example, dibenzylidene acetone does not undergo the slightest change by prolonged heating in dekalin of boiling point, 185–195° C.

<sup>2</sup> *Ber.*, 37, 1147 (1904).

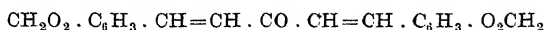
by heating for 8-9 hours to 180° C.; the resin was reddish brown, hard, elastic and not capable of distillation. It was readily soluble in ether, benzene and homologues, chloroform and similar compounds, tetrahydro-naphthalene, glacial acetic acid, acetone and ethyl acetate; moderately soluble in oil of turpentine and fatty oils, and insoluble in alcohol and petroleum ether. It melted between 85° and 95° C.

*Dianisylidene-acetone,*



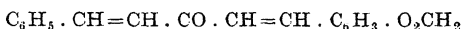
was converted by heating for 6 hours to 220-225° C., into a reddish brown, brittle resin of approximately the same solubility as the one just mentioned; it softened at about 70° C., and was completely melted at about 100° C.

*Dipiperonylidene-acetone,*



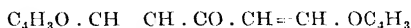
was converted into resin by heating for quite a short period to 260° C. The resin was dark reddish brown, brittle, and melted between 155° and 170° C. Its other properties were similar to those of the above-described resins.

*Benzylidene-piperonylidene-acetone,*



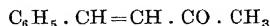
was converted into resin by heating for 4-5 hours at 200° C. The resin was reddish brown, brittle and transparent, and melted at 70-80° C.

*Difural-acetone,*



was converted by heating for 4-5 hours at 200-210° C. into a blackish brown, elastic, hard, lustrous resin, melting at 55-75° C., which was only very slightly soluble in ether.

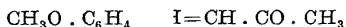
*Benzylidene-acetone,*



was converted into resin by heating for about 12 hours to

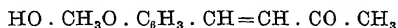
230–240° C. The resin was reddish brown, moderately hard, melted at 60–65° C., and showed the same solubility.

*Anisylidene-acetone*,



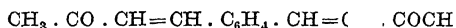
was converted by heating for 4 hours at 220–225° C., into a reddish yellow, hard, elastic, transparent resin, easily soluble in benzene hydrocarbons and in chlorinated methane hydrocarbons, acetone and ethyl acetate, moderately soluble in tetraline, only slightly soluble in oil of turpentine, ether and alcohol, and insoluble in petroleum ether.

*Vanillal-acetone*,



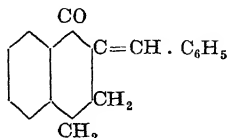
is converted, by heating for about 2 hours to about 230° C., into a reddish brown, hard, elastic resin which melts at 60–80° C., and is easily soluble in chlorinated hydrocarbons such as chloroform, in acetone, and also in dilute alkali.

1–4 di- ( $\gamma$ -keto- $\alpha$ -butenyl) -benzene,



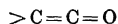
is converted by heating for about 1 hour to 210° C., into a reddish brown, hard, elastic, transparent resin, which melts approximately between 129° and 133° C., and is easily soluble in chlorinated methane hydrocarbons, only slightly soluble in benzene and homologues, acetone, tetraline, glacial acetic acid and fatty oils, and insoluble in alcohol, petroleum ether and oil of turpentine.

*Benzylidene- $\alpha$ -tetralone*,

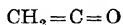


is converted by heating for 20 hours to 270–280° C., into a dark, hard, elastic resin of melting point 75–90° C.

The so-called ketene group,

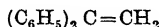


is also of special interest. It may be considered as an unsymmetrically substituted methylene linkage. The simplest complex of this kind is represented by so-called ketene,



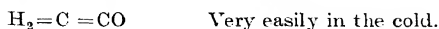
of which there are numerous derivatives.

Theoretically, the replacement of two atoms of hydrogen of the ethylene linkage by the electro-negative oxygen atom might be expected to induce a relatively moderate tendency to polymerization, analogous to the behaviour, for example, of diphenylethylene,



but actually the ketenes, almost all of them show a particularly strong tendency to conversion into dimeric products (1,3-diketo-cyclobutanes), and to some extent into trimerides and higher polymerides.<sup>1</sup> Although the oxygen saturates two valencies of the carbon atom, it thus acts in the manner which one associates with the addition of a monovalent negative substituent in the ethylene linkage. It is interesting to note that similar relations occur in the case of diphenylethylene (see page 95), although in this case two new linkages are undoubtedly saturated.

Although ketenes are of no importance as raw materials for artificial resins, they are of great interest in so far as they illustrate particularly well the influence of substitution on the capacity for polymerization. From this standpoint, the following summary by H. Staudinger is of special interest. Thus, the following groups polymerize as follows—



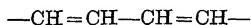
<sup>1</sup> See *Chemie in Einzeldarstellungen*, published by J. Schmidt, Vol. I, H. Staudinger, *Die Ketene*, Stuttgart (1912), pp. 38 *et seq.*

$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{H} \end{array} > \text{C}=\text{CO}$	Very easily
$\begin{array}{c} \text{C}_2\text{H}_5 \cdot \text{OOC} \\   \\ \text{C}_2\text{H}_5 \end{array} > \text{C}=\text{CO}$	Very easily
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH} \end{array} > \text{C}=\text{CO}$	Easily.
$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ \text{C}_2\text{H}_5 \end{array} > \text{C}=\text{CO}$	Slowly.
$\begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_5 \end{array} > \text{C}=\text{CO}$	Slowly.
$\begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{C}_6\text{H}_5 \end{array} > \text{C}=\text{CO}$	Very slowly.

Replacement by halogens increases the tendency to polymerize very considerably. Thus, for example, ethylchlor-ketene<sup>1</sup> is very reactive even at  $-80^\circ \text{C}$ .

### CONJUGATED CARBON DOUBLE LINKAGES

**Hydrocarbons.** If substances contain several carbon double linkages, a very high capacity for polymerization, together with increased reactivity in other directions, is only noticed if so-called conjugated linkages occur as in the following characteristic group—



The second double linkage, occurring in conjunction with the first, therefore acts as a negative substituent, such as halogen, phenyl, carboxyl, and so forth. The reactivity is, therefore, similarly dependent on the character of the substituent. It must be admitted that its effect is in some cases much less marked than in others. Therefore, the resinophoric effect is not of very definite character.

The simplest members of this group, such as,

BUTADIENE.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
ISOPRENE.	$\text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{CH}=\text{CH}_2$
DIMETHYLBUTADIENE.	$\text{CH}_2=\text{C}(\text{CH}_3) \cdot \text{C}(\text{CH}_3)=\text{CH}$

and so forth, are characterized by very great capacity for polymerization. When this occurs the resinoid condition is

<sup>1</sup> See *J. Houben-Meerwein*, Vol. 2, p. 619.

easily overstepped, and rubber-like substances are obtained,<sup>1</sup> of which the so-called "heat-rubber," "acetic acid rubber," and "sodium rubber" (so-called after the polymerizing agents used) attained considerable importance for a time. Recent work by J. R. Katz<sup>2</sup> has shown that essential differences exist in the colloidal character of the artificial rubbers so obtained, on the one hand, and that of the natural products on the other, so that one is not justified in speaking of a complete synthesis of rubber. Regarding the capacity for polymerization of the raw materials used, and in order to thus obtain a comparison of the activity of the compounds further to be described, it may be mentioned that, according to German patent 235,423, it is necessary for the conversion of butadiene or its solution in benzene into rubber, to heat it in an autoclave for 10 hours to 150° C. At 100° C. the reaction requires 4 days. Transformation occurs in part instantaneously when using certain catalysts, even at the ordinary temperature. By using other suitable catalysts, resinous polymerides were obtained.

Thus, butadiene and its homologues<sup>3</sup> were converted in a very short time by boron halides into products which were soluble in benzene, chloroform and ether, insoluble in alcohol, and had the characteristics of artificial resins.<sup>4</sup> The products

<sup>1</sup> See Harries, *Ann.*, 383, 157 (1911); W. H. Perkin, *J. Soc. Chem. Ind.*, 31, 616 (1912); *Kunstst.*, 2, 304 (1912); German Pats. 235,423 (1909), 235,686 (1909); British Pat. 24,790 (1910); see also Summary of Patent Position in *Kunstst.*, 4, 47, 69 (1914); 5, 123, 137 (1915). Also C. D. Harries, *Kautschuk*, Berlin (1919); see also R. Pummerer, *Angew.*, 40, 1168 (1927).

<sup>2</sup> *Kolloidchem. Beih.*, 23, 344 (1926).

<sup>3</sup> Mixtures of ethylene hydrocarbons, such as trimethylethylene, with hydrocarbons containing less hydrogen (with at least two double linkages), such as isoprene, also form soluble products with catalysts of the type  $\text{MCl}_3$ , which are recommended as substitutes for natural resins, such as mastic and shellac. See Chem. Fabrik auf Aktien (vorm E. Schering), German Pat. 278,486 (1913); *Kunstst.*, 4, 358 (1914).

<sup>4</sup> German Pat. 264,925 (1912); see *Kunstst.*, 3, 414 (1913). It should be noted that resinous materials can also be obtained from rubber. Thus, plastic resinous masses are obtained from natural rubber on treatment, for example, with trichloroacetic acid (U.S. Pat. 1,642,018), and also with suitable haloids or halogenides (French Pat. 615,195, British Pat. 285,071), to which phenols may also be added (British Pat. 282,778). Varnish resins, so-called "Thermoprenes," are obtained from rubber by the action of aromatic sulphonic acids or their chlorides; see H. L. Fisher, *Ind. Eng. Chem.*, 19, 1325, 1328; *C.* (1928), I, 1464; H. Gray, *Ind. Eng. Chem.*, 20, 156 (1928); *Chem. Trade Journ.*, 82, 232 (1928); see also *Gummi-Ztg.*, 42, 857, 911 (1928); *Farben-Ztg.*, 33, 1474 (1927-28); *Farbe und Lack* (1928), 62, 186; see also Goodrich Co., U.S. Pat. 1,668,235-7; *C.* (1928), II, 192.

were syrupy, viscous, soft, plastic, crumbly or brittle according to the applied temperature and the proportions of the ingredients. The colour varies from almost colourless to a deep brown. These products in no way resemble rubber, and their use is proposed as resin or shellac substitutes.

With increasing substitution of butadiene by alkyl or aryl groups, the rubber-like character of the polymerides is weakened, and resin formation becomes more marked. This behaviour may be explained by steric hindrance to polymerization and to influences of a physical and chemical character, which naturally affect the derivatives of high molecular weight with regard to viscosity, hardness and solubility. Thus, for example, 2,3-diethyl-butadiene and 1-phenyl-butadiene form resinous or tarry products on heating in a sealed tube under ordinary conditions.<sup>1</sup>

1 *phenylbutadiene*,



is a strongly refractive liquid with an odour of styrol, of boiling point 95° C. at 20 mm. pressure, which polymerizes on distillation under atmospheric pressure into products of high boiling point and which resinifies in the air by polymerization with reduction of density.<sup>2</sup> If phenylbutadiene is heated to 150–155° C. in the presence of hydrogen,<sup>3</sup> or boiled with pyridine,<sup>4</sup> bis-phenylbutadiene is formed.

1-*phenyl-4-methylbutadiene*,



polymerizes on standing to form a viscous liquid which is not soluble in ether to a clear liquid.<sup>5</sup> Similar results are obtained with other homologues.<sup>6</sup>

<sup>1</sup> See *Kunstst.*, 4, 324 (1914).

<sup>2</sup> Klages, *Ber.*, 35, 2650 (1902); 40, 1769 (1907); Liebermann, Rüber, *Ber.*, 35, 2697 (1902).

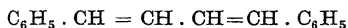
<sup>3</sup> Rüber, *Ber.*, 37, 2274 (1904); see also Liebermann, Rüber, *loc. cit.*

<sup>4</sup> V. d. Heide, *Ber.*, 37, 2103 (1904).

<sup>5</sup> Klages, *Ber.*, 40, 1769 (1907).

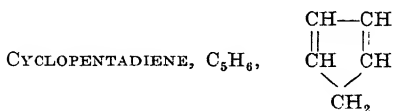
<sup>6</sup> See Grignard, *C.* (1901), II, 625; *Ann. chim.*, (7), 24, 486; Beilstein, V, 521, *et seq.*

In contrast to the above-mentioned substitution products of butadiene, symmetrical *diphenylbutadiene*,



shows much less tendency to polymerization, which is explicable as it may occur in three stereo-isomeric forms, by which means considerable possibilities for the saturation of residual valencies within the molecule appear to occur. By prolonged heating for 10 hours at the very high temperature of  $340^\circ \text{C}$ . in a current of carbon-dioxide, a black, lustrous, hard and elastic resin, melting between  $60^\circ$  and  $80^\circ \text{C}$ ., and soluble in benzene, chloroform, and so forth, could be obtained.<sup>1</sup> It is, however, difficult to assume that polymerization only is induced by treatment of such an energetic character.

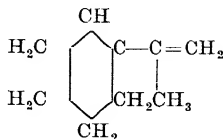
Even when conjugated double bonds occur in cyclic compounds, they are associated with considerable power of polymerization.<sup>2</sup> As examples, we may mention the behaviour of such compounds as cyclopentadiene, cyclohexadiene, and so forth. The main influence of the cyclic character of these compounds on the properties of the polymerides is probably shown by the production of products of a resinoid, rather than of a rubber-like, character, that is, of amorphous pulverizable products.



polymerizes at the ordinary temperature to dicyclopentadiene, a crystalline substance easily soluble in alcohol, ether, and

<sup>1</sup> W. Herzog, J. Kreidl, *Angew.*, 36, 473 (1923).

<sup>2</sup> This is the case even if they are only partially within the ring, as in the following compound—



(see Harries, *Angew.*, 36, 473 (1923); German Pat. 235,



ligroin, of melting point  $32.9^{\circ}\text{C}$ .<sup>1</sup> On heating in a sealed tube to  $160^{\circ}\text{C}$ ., a yellow, amorphous, insoluble polymeride is produced which can be depolymerized to cyclopentadiene by heating.<sup>2</sup> Concentrated sulphuric acid and fuming nitric acid act on cyclopentadiene with explosive violence with charring or combustion.<sup>3</sup> The dimeride is also attacked explosively by concentrated sulphuric acid. It is resinified by dilute acid.<sup>4</sup>

Detailed investigations have been carried out by H. Staudinger and his pupils, A. Rheiner and H. A. Bruson.<sup>5</sup> These showed that a deep-seated difference exists between those polymerides which are obtained by heating, and those obtained at low temperatures under the influence of certain catalysts. According to the first-named processes, polymerides of uniform character could easily be obtained, those of higher molecular weight being obtained with longer and more intensive heating. A separation could be effected by distilling off the dimeride and trimeride in a high vacuum at temperatures up to  $100^{\circ}\text{C}$ ., and separating these products by further distillation at 10 mm. pressure. From the residue the tetrameride was extracted with ether, and the pentameride with boiling benzene and xylene. The insoluble polycyclopentadiene remained as a residue. The following summary describes the formation and characteristics of the various polymerides—

Dicyclopentadiene, see above.

Tricyclopentadiene is obtained by heating for 14 hours to  $150\text{--}160^{\circ}\text{C}$ ., b. p (3 mm.)  $105^{\circ}\text{C}$ .; easily soluble in ether and petroleum ether, slightly soluble in alcohol and methyl alcohol—very slightly soluble in glacial acetic acid; small needles; it distils, partially undecomposed, at the ordinary pressure.

Tetracyclopentadiene is obtained, together with the pentameride, by heating for 22 hours to  $170\text{--}180^{\circ}\text{C}$ . It is obtained from ethyl acetate in micro-crystalline form. It is easily soluble in cold ether, benzene, and chloroform, and in hot petroleum

<sup>1</sup> Étard; Lambert, *Compt. rend.*, 112, 945 (1891); Kraemer, Spilker, *Ber.*, 29, 554, 557 (1896); compare *Beilstein*, V, 496.

<sup>2</sup> Kronstein, *Ber.*, 35, 4151 (1902).

<sup>3</sup> Kraemer, Spilker, *loc. cit.*

<sup>4</sup> Boes, *C.* (1902), II, 32; compare *Beilstein*, V, 496.

<sup>5</sup> *Helv. Chim. Acta*, 7, 23; *C.* (1924), I, 1780; *Ann.*, 447, 97, 110; *C.* (1926), I, 3465, 3466.

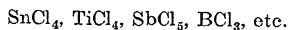
ether or ethyl acetate. It is insoluble in alcohol and ethyl alcohol.

Pentacyclopentadiene is formed in the same manner as the tetrameride. It is obtained from benzene as a white powder of melting point  $270^{\circ}\text{C}$ . It is very slightly soluble in the cold, and soluble in the heat in benzene, toluene, xylene, chloroform, carbon disulphide, pyridine and nitro-benzene, and is insoluble in alcohol, methyl alcohol, ether and petroleum ether. It can be sublimed without decomposition under a high vacuum.

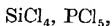
Polycyclopentadiene is probably a six-fold or seven-fold polymer. It is obtained by heating for 90 hours to  $200^{\circ}\text{C}$ . When free from lower polymers, the product forms an insoluble, white or slightly grey powder, which melts at about  $373^{\circ}\text{C}$ . with decomposition. It is very slowly attacked by concentrated boiling nitric acid, does not react with bromine, and forms cyclopentadiene on heating to  $500^{\circ}\text{C}$ .

It is interesting to note that according to the X-ray investigation of E. Ott, the insoluble polymer is also crystalline, and shows the same X-ray diagram as the tetrameride and pentameride.

A polymeride which is entirely different from the above-described products is obtained by the action of certain catalysts, such as



On the other hand, definitely acid chlorides, such as



and acetyl chloride are inactive.<sup>1</sup> Thus, on treating cyclopentadiene in chloroform solution at  $-5^{\circ}$  to  $-10^{\circ}\text{C}$ . with a little  $\text{SnCl}_4$ , a polymeride is obtained in a few minutes, which after purification and drying forms a white amorphous powder of molecular weight, 1,300–6,700. It is soluble in benzene, chloroform, carbon tetrachloride and carbon disulphide to a slightly viscous liquid, and is also slightly soluble in alcohol, ether and acetone. This polymeride also absorbs oxygen from

<sup>1</sup> The active catalysts also polymerize indene, cumarone, styrol, isoprene and Chinese wood oil, but do not polymerize acrylic and cinnamic esters and vinyl bromide.

the air with extreme ease with formation of an oxide  $(C_5H_6O)_x$ , which is an insoluble amorphous powder of deep yellow, orange yellow, or brownish colour, which becomes dark in colour on heating to over  $160^\circ C.$ , and decomposes at over  $300^\circ C.$  Regarding the constitution of these polymerides, see footnote 1 page 63.

Similar polymerizing power is shown by the cyclic homologues of cyclopentadiene<sup>1</sup> and by the corresponding alkylated products.<sup>2</sup> The reactivity of cyclohexadiene, for example, is, however, considerably less than that of the open-chain butadienes, and is not even as marked as that of cyclopentadiene.

Thus, according to F. Hofmann and P. Damm<sup>3</sup> on heating cyclohexadiene for 10 hours to  $200$ – $220^\circ C.$ , in a sealed tube, polymerides are formed containing 55 to 65 per cent of the dimeride, and only 30 to 40 per cent of higher polymerides. The dimeride has the characteristics of terpenes. The more highly polymerized product is a white, odourless powder which sinters at about  $75^\circ C.$ , becomes vitreous at about  $90^\circ C.$ , and forms opaque droplets at about  $105^\circ C.$  When fresh it is easily soluble in benzene and chloroform, insoluble in alcohol, acetone and glacial acetic acid, and very oxidizable in the air. The product can be separated into constituents varying in solubility. A polymeride of somewhat different properties can be obtained by the action of ferric chloride as a catalyst without external heating. Additions of sodium or of sodium and carbon dioxide have no effect.

For the production of resinous products of very valuable properties, the following process has been recommended.<sup>4</sup> Condensing agents, such as sulphuric acid or alkali metals, are caused to act under the influence of heat in a suitable manner (dilution, small quantities, successive additions, and so

<sup>1</sup> On cyclohexadiene, see Harries, *Ber.*, 42, 693 (1909); on cycloheptadiene, see Willstätter, *Ann.*, 317, 231 (1901); on the polymerizing capacity of the cyclo-octadiene (1·5), containing no conjugated double linkage, see Willstätter, Veraguth, *Ber.*, 38, 1979 (1905); Harries, *Ber.*, 41, 672 (1907).

<sup>2</sup> On alkylated cyclohexadienes, see Harries, *Ber.*, 34, 303 (1901); Auwers, Hessenland, *Ber.*, 41, 1824 (1908).

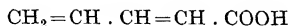
<sup>3</sup> *Mitt. aus dem Schlesischen Kohlenforschungsinstitut d. Kaiser Wilhelm-Ges.*, 2, 97 (1925); *C.* (1926), I, 2342, etc.

<sup>4</sup> German Pat. 263,159 (1912); see *Kunstst.*, 3, 373 (1913); *C.* (1913), II, 1091.

forth) on dihydrobenzene, its homologues, the derivatives and cycloisomerides of these substances or of products which are convertible into such substances, such as dichlor-cyclohexane. The products are solid, transparent, vitreous masses, easily soluble in benzene, oil of turpentine, and so forth, which form strongly adherent varnishes.

To the hydrocarbons here dealt with, containing conjugated double linkages, a whole series of compounds must be added, the constitution of which is to some extent still unknown, but of which it is known that they form resinous or pitch-like products under the above-described conditions. To this class belong, for example, certain constituents of cracked mineral oils, which frequently undergo resin-forming polymerization,<sup>1</sup> in which, however, oxidation processes seem to play a part.<sup>2</sup> Moreover, the formation of acid resins and acid tars in general appears to depend essentially on the presence of such unsaturated hydrocarbons. Finally, we must refer to a group of compounds produced by chlorination followed by fission of hydrochloric acid, by which means highly unsaturated hydrocarbons are formed, which are convertible into resins by polymerization.<sup>3</sup>

**Carboxylic Acids and Esters.** The presence of a carboxyl group adjoining the conjugated double linkage has a much slighter effect than in the case of the ethylene linkage. Thus, even in the case of the simplest representative of this group,  $\beta$ -vinyl-acrylic acid,



scarcely any increase in reactivity can be observed, the conditions for polymerization being somewhat similar to those for butadiene.

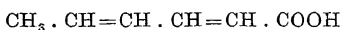
<sup>1</sup> See Ellis, Wells, *J. Ind. Eng. Chem.*, 7, 1029 (1915); Brooks, *Chem. Met. Eng.* (1921), 1024; Brooks, Humphrey, *J. Am. Chem. Soc.* (1918), 852; U.S. Pat. 1,318,060; 1,318,061 (1919); see C. Ellis, *Synth. Resins*, p. 66 *et seq.*; British Pat. 138,046 (1919); *Kunstst.*, 10, 158 (1920); U.S. Pat. 1,324,649 (1919).

<sup>2</sup> See Smith, Cooke, C. Ellis, *Synth. Resins*, p. 66.

<sup>3</sup> See German Pat. 263,159; German Pat. 343,466 (1915); American Pats. 1,384,423, 1,384,447; *C.* (1921), IV, 1250. The American Patents deal with the manufacture of drying oils (Bielouss, Gardner).

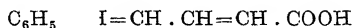
*β-vinyl-acrylic acid* polymerizes slowly on standing, and rapidly on heating to 130° C., to an amorphous, adhesive product, which dries to tough crusts in the air, becomes brown at 140° C., decomposes at 300° C., and is scarcely soluble in boiling sodium hydroxide or sodium carbonate solutions.<sup>1</sup> The reactivity of the esters seems to be greater, as may be deduced from their employment as linseed oil substitutes.<sup>2</sup>

Its homologue, *sorbinic acid*,



is capable of polymerization in the form of its esters; thus, the ethyl ester is converted on standing into a viscous oil.<sup>3</sup> In the utilization of sorbinic acid ester as a drying oil<sup>4</sup> it is probable that the capacity for polymerization plays a certain part, although oxidation processes possibly assist. *α*-Methyl- and *α*-ethyl-sorbinic acids are converted into adhesive masses on standing in a desiccator.<sup>5</sup>

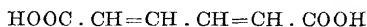
*Cinnamal-acetic acid*,



occurs in a low-melting and a high-melting form, and shows no marked tendency to polymerization. The ethyl ester, however, forms an oil which cannot be distilled, a fact which may be due to polymerizing tendencies.<sup>6</sup>

*Cyclohexadiene-carboxylic acids* are decomposed on heating, with liberation of carbon dioxide, which is followed by further reactions. However, the methyl ester, for example, of 1·4-dimethyl-cyclohexadiene-1·3-carboxylic acid (2), is an oil which gradually becomes more viscous.<sup>7</sup>

*Muconic acid*,



<sup>1</sup> Döbner, *Ber.*, 35, 1137 (1902); compare *Beilstein*, II, 481.

<sup>2</sup> German Pat., 389,086.

<sup>3</sup> Vorländer, Weissheimer, Sponnagel, *Ann.*, 345, 228 (1906).

<sup>4</sup> German Pat. 389,086 (1922); *C.* (1924), I, 1717; *Kunstst.*, 14, 26, 72 (1924).

<sup>5</sup> See *Beilstein* II, 486, 489.

<sup>6</sup> See *Beilstein*, IX, 639.

<sup>7</sup> Auwers, *Ber.*, 41, 1831 (1908).

is not capable of polymerization, and therefore resembles to a certain degree diphenyl-butadiene, of corresponding constitution. On the other hand, on heating its esters for 5 hours to 180° C. in a sealed tube, dimerides are formed, together with black, pitch-like masses which are easily soluble in alcohol, acetone and ethyl acetate, but are insoluble in benzene, ligroin, carbon disulphide and chloroform.<sup>1</sup>

**Aldehydes and Ketones.** Among substances containing a carbonyl group in a position adjoining the conjugated double linkage, those of aldehydic character are but little known.<sup>2</sup> On the other hand, numerous ketones exist containing the characteristic group

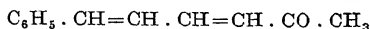


Such substances as *sorbinic acid-methyl ketone*,

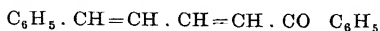


its homologues, and so forth, resinify in the air and on exposure to light, although it is not known to what extent this is due to polymerization processes.<sup>3</sup> The possibility of such reactions was shown by the investigations of W. Herzog and J. Kreidl<sup>4</sup> on arylated ketones.

Thus, resins were obtained, which must be considered as products of polymerization, on heating *cinnamylidene-acetone*,



for 6 hours to 220° C. in a stream of carbon dioxide, on heating *cinnamylidene-acetophenone*<sup>5</sup>



<sup>1</sup> Kurt Vogt, *Mitt. aus dem Schlesischen Kohlenforschungsinstitut d. Kaiser Wilhelm-Ges.*, 2, 69 (1925); *C.* (1926), I, 2341.

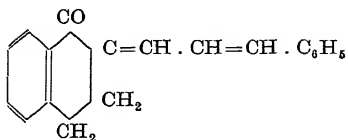
<sup>2</sup> Compare, however, the vinylen homologues of furoil (W. König, *Ber.*, 58, 2559 (1915), and cinnamic aldehyde (Vorländer, Fischer, Kunze, *Ber.*, 58, 1284 (1925), which show a strong tendency to resinification, possibly due to polymerization and condensation.

<sup>3</sup> See *Beilstein*, I, 750, *et seq.*

<sup>4</sup> *Angew.*, 35, 465, 641 (1923); German Pat. 397,603; *Kunstst.*, 14, 155 (1924); *C.* (1924), II, 1412.

<sup>5</sup> On the action of light on nitro-derivatives, see M. Giua, *C.* (1926), I, 639 (Resinification).

for 2 hours to 190–200° C., and on heating cinnamylidene- $\alpha$ -tetralone,



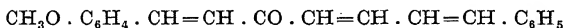
for a few minutes to about 230° C. An exceptionally strong power of polymerization on heating is also shown by such compounds as dicinnamylidene-acetone,



piperylidene - cinnamylidene - acetone and fural - cinnamylidene-acetone, which are polymerized with a strongly exothermic reaction at 180° C., 210° C. and 190–200° C. respectively, forming soluble resins melting at the fairly high temperature of about 130° C. It was further found that heating for quite a short period to 220° C. in a stream of carbon dioxide sufficed to convert compounds, such as benzylidene-cinnamylidene-acetone,

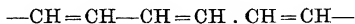


or anisylidene-cinnamylidene-acetone,



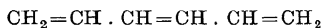
into resinous polymerides of high melting point.

In a similar manner, three or more conjugated double linkages,



are associated with a very high reactivity.

Thus, hexatriene,



polymerizes partially on standing; with concentrated sulphuric acid it immediately forms a solid polymer.<sup>1</sup>

<sup>1</sup> Perkin, *J. Chem. Soc.*, 91, 814 (1907); compare *Beilstein*, I, 263.

The corresponding products, such as vinylene homologues of cinnamic aldehydes<sup>1</sup> and furoles,<sup>2</sup> tend to form resins on standing or distilling. A similar activity is also shown by wood oil (tung oil) or elaeostearic acid, as is more particularly shown in the rapid production of stand oil from the former material.<sup>3</sup>

The entry of negative substituents into trebly or more highly conjugated double compounds removes the capacity for polymerization, as is shown by the behaviour of the diphenyl-polyenes.<sup>4</sup>

**Substances with other Unsaturated Linkages.** Apart from carbon double linkages, the carbonyl group,



and the azomethine group,



play the most important part as unsaturated groups which give rise to polymerization, whilst the nitrile group<sup>5</sup> need not be considered here.

**Carbonyl Group.**<sup>6</sup> The carbonyl group is a typical constituent of aldehydes, ketones and carboxylic acids. With regard to the aldehydes, their simplest representative, formaldehyde,  $CH_2O$ , is characterized by the capacity of entering

<sup>1</sup> Vorländer, E. Fischer, K. Kunze, *Ber.*, 58, 1284 (1925).

<sup>2</sup> W. König, *Ber.*, 58, 2559 (1925).

<sup>3</sup> Thus, wood oil is converted at 285° C., within about 10 minutes into a jelly which can be cut (test for wood oil). It is to be noted that wood oil can be polymerized by iodine, and more particularly by tin tetrachloride and substances of similar character; see J. Marcusson, *Angew.*, 33, 234 (1920); H. Staudinger and H. A. Bruson, *Ann.*, 447, 97, 110 (1926). On quantitative wood oil polymerization, see Boughton, *Seifensieder-Ztg.* (1909), 1031; J. Marcusson, *Angew.*, 39, 478 (1926); J. Scheiber, *Farbe und Lack* (1928), 274, 286.

<sup>4</sup> R. Kuhn, A. Winterstein, *Helv. chim. Acta*, 11, 87 (1928); *C.* (1928), I, 1401.

<sup>5</sup> On the spontaneous resinification of cyanacetyl chloride, see G. Schroeter, *Angew.*, 40, 1369 (1927). On polymeric malonitriles, see R. Schenck, H. Finken, *Ann.*, 462, 267 (1928).

<sup>6</sup> In carbon monoxide the carbonyl group appears, so to say, in the free state, according to the usual structural formulae. Actually, however, the carbonyl group, as it occurs in compounds of the type of aldehydes, ketones, and possibly of carboxylic acids, should not be considered as identical with carbon monoxide. See, however, H. Scheibler, *Angew.* (1927), 1072.



into very varying polymerization processes, as polymers varying in character can be obtained according to the nature of the exciting agent. Regarding their probable constitution, see page 65. Acetaldehyde,  $\text{CH}_3 \cdot \text{CHO}$ , readily forms a dimeride with marked power of association (metaldehyde). A trimeride can also be obtained, which is known as paraldehyde. In the case of the higher aldehydes, the capacity for forming the higher polymeric forms rapidly decreases. It is possible to prepare trimerides of the same type as paraldehyde, which are produced like that substance under the influence of catalysts, such as sulphuric acid, hydrochloric acid, sulphur dioxide, calcium chloride, zinc chloride, and so forth. Such derivatives are known from propionic aldehyde, the various butyric aldehydes, trimethyl-acetaldehyde, isovaleraldehyde, oenanthaldehyde, phenyl-acetaldehyde,<sup>1</sup> and so forth. All these substances are liquids or well crystallizing products of low melting point. Halogenated aldehydes, such as chlor-acetaldehyde, dichlor-acetaldehyde,  $\beta$ -chlorpropionic-aldehyde, and so forth, also readily form paraldehydes; in some cases, indeed, apparently spontaneously, in consequence of the liberation of minute quantities of halogen hydrides.

*Benzaldehyde* was converted into a resinous polymeride by prolonged exposure to light throughout the whole of one summer. After purification, this polymeride melted at  $125\text{--}130^\circ \text{C.}$ , and showed a molecular weight corresponding to  $(\text{C}_7\text{H}_6\text{O})_9$  in benzene solution.<sup>2</sup>

*Dialdehydes* and *aldols* show a strong tendency to form polymers. Dialdehydes, such as glyoxal, succinic aldehyde, adipic-dialdehyde, suberic dialdehyde, and so forth, frequently form polymers of high molecular weight. Thus, suberic dialdehyde,



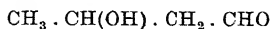
forms rubber-like masses on standing which gradually become very hard. The product is reconverted into the monomolecular aldehyde on distillation, or on boiling with dilute sulphuric

<sup>1</sup> Regarding velocities of polymerization, see C. J. Enklaar, *Chem. Weekblad*, 23, 174 (1926); *C.* (1926), II, 192.

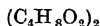
<sup>2</sup> Ciamician, Silber, *Ber.*, 36, 1575 (1903); see also *Ber.*, 42, 1387 (1909); . . regarding various other aldehydes, see *Ber.*, 34, 1538 (1901).

acid.<sup>1</sup> O-phthallic aldehyde is converted rapidly on exposure to light into a white, crumbly mixture of various compounds.<sup>2</sup>

Acet-aldol,



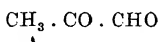
becomes viscous on standing in the warmth, being polymerized to paral-  
dol,



This behaviour is a quite general characteristic of aldols.<sup>3</sup>

The *ketones* do not usually show any tendency to polymerization. Exceptions are formed by methyl-cyclopropyl ketone (see page 106) and diacetyl (see below), which occur in polymeric forms.<sup>4</sup> The formation of diacetone-alcohol from acetone under the influence of alkali must also be mentioned.

An increased capacity for polymerization is found in the case of those ketones and aldehydes which may also occur in enolic forms.<sup>5</sup> In these cases, however, the cause of the formation of polymers is primarily due to the ethylenic linkage which is then formed. It is probable that phenomena of this kind play a part in the process of drying fatty oils.<sup>6</sup> Among the simpler compounds the following must be classified in this group: Methylglyoxal,



which forms a vitreous, very hygroscopic polymeride,



diacetyl,



which polymerizes partially to the trimolecular crystalline

<sup>1</sup> Baeyer, *Ber.*, 30, 1963 (1897).

<sup>2</sup> Thiele, Günther, *Ann.*, 347, 107 (1906).

<sup>3</sup> L. Kohn, *Monatsh.*, 21, 80 (1900).

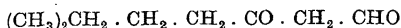
<sup>4</sup> Diels, Jost, *Ber.*, 35, 3290 (1902).

<sup>5</sup> See *Ber.*, 59, 108 (1926).

<sup>6</sup> See J. Scheiber, *Farbe und Lack* (1926), 295; (1927), 75; *Angew.*, 40, 1279 (1927).

<sup>7</sup> Harries, Türk, *Ber.*, 38, 1632 (1905).

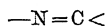
diacetyl by the prolonged action of ice-cold concentrated hydrochloric acid;<sup>1</sup> isocaproyl-acetaldehyde,



which polymerizes very easily;<sup>2</sup> 1,3-dimethyl-cyclohexene (3)-on (5), and 1 metho-ethyl-cyclohexene (2)-on (4), which both form crystalline dimerides.<sup>3</sup>

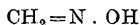
In the case of the *carboxylic acids*, polymerization is shown in the tendency of acetic acid to occur in dimolecular form. In the case of chloroacetic acid, the formation of three or four modifications may also be considered as an indication of a certain capacity for polymerization. The conjunction of two carboxyl groups as in oxalic acid also seems to cause a certain tendency to polymerize.

**Azomethine Group.** The typical atomic linkage of the azomethine group,

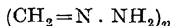


undoubtedly shows a marked capacity for polymerization, as may be concluded from the behaviour of the following substances—

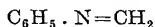
Formaldoxime,



polymerizes gradually at the ordinary temperature and less easily at higher temperatures.<sup>4</sup> *Formalhydrazine*,



is only known in the polymerized condition. *Anhydro-formaldehyde-aniline*,



occurs as a dimeride, and is apparently polymerized by prolonged heating to a high temperature.

Böhler<sup>5</sup> heats anhydro-formaldehyde-aniline for 10 to 12

<sup>1</sup> Diels, Jost, *Ber.* 35, 3290 (1902).

<sup>2</sup> Couturier, Bongert, *Compt. rend.*, 140, 1696 (1905).

<sup>3</sup> See *Beilstein*, VII, 61-63.

<sup>4</sup> Dunstan, Bossi, *J. Chem. Soc.*, 73, 353 (1898); Scholl, *Ber.*, 24, 575 (1891).

<sup>5</sup> German Pat. 335,984 (1917); *C.* (1921), IV, 196; *Kunstst.*, 11, 118, 142 (1921); Austrian Pat. 80,202; *Kunstst.*, 10, 150, 215 (1920).

hours to 130–140° C., and so obtains a clear resilient resin, with evolution of a vapour forming a heavy white fog. This resinous product has the valuable new property of increasing the solubility of natural and artificial resins which are otherwise difficult to dissolve or incompletely dissolved, and also to increase their lustre, hardness, and capacity for taking a polish. It also shows the new property, otherwise peculiar to shellac, of not impairing the luminosity of Bengal-lights when burnt, and of ensuring uniform and quiet combustion of the powder. When heating the anhydro-formaldehyde-aniline, the addition of free aniline has been found to be advantageous, as by this means the distillation process is facilitated, and the solubility of the resinous product in solvents other than benzene, for example, in alcohol, is increased. The yield of resin can be increased by the addition of small quantities of acids or alkalies while heating. The two processes can be combined, that is to say, one may add aniline, as well as either acid or alkali, during heating.

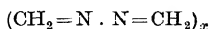
It must, obviously, be assumed that in this process other reactions of unknown character occur, together with polymerization; partial decomposition most certainly occurs. (See also page 155 *et seq.*)

Polymerization can be facilitated by the action of acids; thus, a resin is formed from acetaldehyde and aniline hydrochloride, and is known as Schultz's Base. (See page 67.)

If two azomethine groups are linked together, the following grouping is obtained—

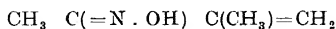


and shows a very considerably increased power of polymerization. Thus, diformalhydrazine,

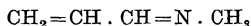


is known in polymeric form only.

Just as the addition of one azomethine group to another increases the power of polymerization, combination with an ethylene group has a similar effect. Thus, 2-methyl-butene-(1) oxime (3),

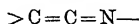


is known not only in the monomeric, but also in the dimeric and trimeric forms. The polymeric crystalline products are reconverted into the monomolecular compound on distillation in the air or on heating with sulphuric acid. According to P. Silberrad, *acroleinmethylamine*,

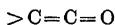


can be polymerized to form a rubber-like product, known as "pyrido" rubber.<sup>1</sup>

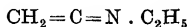
The behaviour of the grouping,



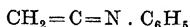
which must be considered as an analogue of the group,



and which represents the typical complex of the ketene-imines, is of special interest. The simple representatives, such as ketene-ethylimine,

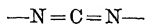


and ketene-phenylimine,

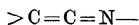


are extremely rapidly polymerized to resinous substances even on standing for a short time. Ketene-imines in which the ethylene group is substituted are not so reactive.<sup>2</sup>

The grouping,



is also of special interest, as it has been designated as a resinophoric complex by Herzog and Kreidl.<sup>3</sup> It has undoubted analogies to the group,



the reactivity of which it shares. It is the characteristic group,

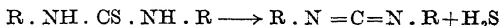
<sup>1</sup> *Gummi-Ztg.*, 25, 1958 (1911).

<sup>2</sup> Staudinger, Hauser, *Helv. Chim. Acta*, 4, 887 (1921).

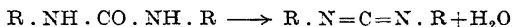
<sup>3</sup> *Angew.*, 36, 472 (1923).

more particularly, of the carbodiarylimides, which were specially investigated by Herzog.<sup>1</sup> These are easily polymerized, and form brown resins which are readily soluble in benzene, chloroform, carbon tetrachloride, trichlorethylene, oil of turpentine, fatty oils, and so forth. The varnishes give lustrous coatings.

According to Herzog, carbodiarylimides can be satisfactorily produced by heating di-substituted thioureas above their melting point, when the following general reaction occurs—

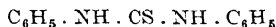


This reaction is accompanied by a small amount of decomposition with liberation of the respective base, for example, aniline. These products can be obtained in a similar manner, but with a larger amount of decomposition, by prolonged heating to a high temperature of the corresponding urea derivatives,



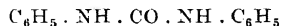
It was found advantageous to carry out the reaction in the presence of a high-boiling solvent, such as aniline. By this process the carbo-di-imides are obtained in the polymerized condition. Some of the crude products can be purified by distillation.

Thus, s-diphenylthiourea,



(melting point 154° C.) forms a brown, brittle, resinous polymeride on heating for 35 to 40 hours to 200–205° C., or for 40 hours in 50 per cent aniline solution under reflux, followed by removal of the separated and added aniline. A portion of this crude product can be distilled at a pressure of 30 mm. at about 219° C. The distillate solidifies to a resinous product on cooling, which appears to be identical with carbodiphenylimide.

This product can also be obtained by heating s-diphenylurea,



for about 40 hours to 235–240° C.

<sup>1</sup> *Oesterr., Chem.-Ztg.*, 24, 76 (1921), where the older literature will be found; see also Ellis, *Synthetic Resins*, pp. 243, 245, etc.

Similar resins were obtained from s-di-o-tolylurea, s-di-p-tolythiourea, s-phenyl-p-tolythiourea, s-di-p-chlorphenylthiourea, s-allyl-phenylthiourea, s-dibenzylthiourea, and from the corresponding di- $\alpha$ - and - $\beta$ -naphthyl- and 2,4-dimethylphenyl derivatives.

**Summary.** In any attempt to form a general picture of the decisive conditions for polymerization processes, on the basis of the above-described experimental data, it must naturally be remembered that this is only possible on broad lines. However, certain regularities can be recognized, which may be expressed approximately by the following rules—

1. Broadly speaking, in simple compounds any unsaturated group



acts as a polymerizing factor. The degree of capacity for polymerization is decided mainly by the state of aggregation, but also by the external conditions which are applied, such as pressure, heat, and catalysts.

2. The power of polymerization of the simplest representatives of the various classes is only very slightly influenced by the addition of positive groups in positions otherwise occupied by hydrogen, as long as the number of substituent groups is not too large. At the same time, such substitution in many cases causes the necessary external conditions favouring polymerization to be more easily attained (influence of the state of aggregation).

3. Substitution in the typical group by a negative substituent quite generally causes a considerable increase in the power of polymerization. In the majority of cases, the formation of highly polymeric products is due to this cause.

4. A negative substituent, which is not connected directly with a typical group, exercises practically no influence in the direction of increasing the polymerization. As examples, we may cite allyl-benzene and vinylacetone.

5. *Two* negative substituents attached directly to the typical group usually greatly weaken the power of polymerization. Substances formed in this way may, under the circumstances,

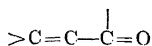
be practically indifferent. When polymerization does occur in such cases it is usually restricted to the formation of dimeric products.

6. Two negative substituents, one of which is directly attached to the typical group, whilst the other is attached by means of a methylene group, act in the same manner as one negative substituent. Therefore an increase of reactivity is to be expected.

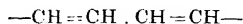
7. When two typical groups occur in association, one of them acts in the same manner as a negative substituent. Consequently, a combination of three typical groups causes no further increase in reactivity, but may even cause a decrease according to rule 5.

8. A divalent negative substituent, such as  $-\text{O}-$ ,  $\text{NH}=\text{}$  or  $\text{NR}=\text{}$  or diphenylene, behaves as a single negative complex, that is, the capacity for polymerization is very considerably increased.

If one considers the reactivity of the so-called resinophoric groups in the light of the experimental material and of the foregoing principles, it is clear that their effect can only be evinced within certain limits.<sup>1</sup> In the group,



the formation of high polymerides is only to be expected if the vinyl-carbonyl group is present. Among substances containing the group,



the butadienes show by far the greatest activity. Azomethine, on the other hand, must be considered as only conditionally active, as the ketenimines are not comparable. These ketenes form a class of particularly active ethylene derivatives. Finally, in carbo-diarylimide, we have a strongly activated azomethine group, the exceptional characteristics of which may be ascribed to the same causes as the increased reactivity of the ethylene group in ketenes and ketenimines.

<sup>1</sup> The opposition to Herzog and Kreidl's views by H. Wolff (*Angew.*, 40, 1010 (1917)) appears to be too far-reaching.



For the purpose of practical resin formation, the choice of raw materials must be made in the light of the above circumstances. If soluble and fusible resins are required, one will choose comparatively complicated substances as raw materials, the reactivity of which ceases with formation of dimeric products, as was done by W. Herzog and J. Kreidl. If, however, it is desired to obtain resinous substances which are capable of being converted into final products, it is a mistake to attempt to achieve this aim by an accumulation of unsaturated linkages and negative substituents. On the contrary, the choice must be limited to substances of as simple a character as possible, as these alone possess the capacity for conversion into highly polymeric and colloidal final products. In practice, of course, this means a very considerable limitation of the possibilities. This is, however, only true with regard to the number of raw materials, for, regarding the polymerizing agencies to be employed, innumerable possibilities remain unexplored and await systematic investigation.

## CHAPTER X

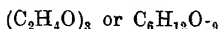
### RESIN-FORMING CONDENSATIONS<sup>1</sup>

**Varieties of Condensation.** In chemistry, the terms "condensation" or "condensation process" indicate reactions in which new products are formed by the liberation of simple atomic groups, such as H, OH, halogen, etc. As the expelled atoms or groups are not capable of free existence as such, but usually unite to form simple substances, such as  $\text{H}_2\text{O}$ ,  $\text{HCl}$ ,  $\text{H}_2$ , and so forth, the by-products formed in this way typically accompany all true condensation processes.

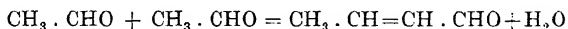
In the case of polymerization, the formula of the product is a mere multiple of that of the monomeride. In condensations, on the other hand, the sum of the atoms forming the liberated compounds must be subtracted from the sum of the constituents taking part in the reaction in order to calculate the formula of the product. Thus, for example, if acetaldehyde,



polymerizes to form the trimeride (paraldehyde), the formula of the product is



If, however, two molecules of acetaldehyde condense to form crotonaldehyde,



the reaction product possesses the formula,



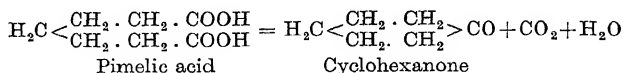
which is no longer a mere multiple of that of the raw material.

Condensation processes may be either intra-molecular or

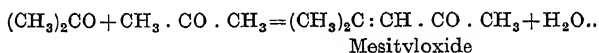
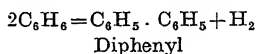
<sup>1</sup> A very full description of condensations is contributed by R. Kempf to J. Houben, *Methoden d. org. Chemie*, Third Edition (1925), II, pp. 716-945. to which we may refer.

extra-molecular. In the latter case, two or more molecules may be concerned, and these may, moreover, be similar or different. We may give the following examples of these various cases—

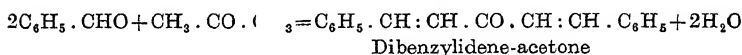
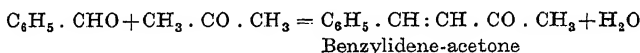
(a) Intra-molecular or internal condensation :



(b) Extra-molecular condensation between similar molecules, or auto-condensation :



(c) Extra-molecular condensation between different molecules :

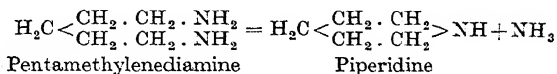
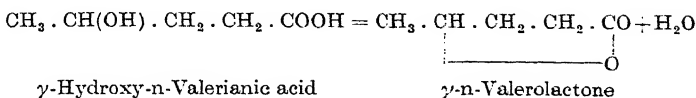


The new linkage can take place in two principal ways. If it occurs between two carbon atoms the process is termed a "condensation" in the narrower sense, or a nuclear condensation. Condensations of any other kind, as, for example, between carbon and oxygen, nitrogen or sulphur, or between oxygen and oxygen, oxygen and nitrogen, nitrogen and nitrogen, and so forth, are characteristic of condensations in the wider sense. This distinction is justified for the reason that carbon-carbon combination is alone distinguished by exceptional stability, and also by the variety of ways in which it may occur.

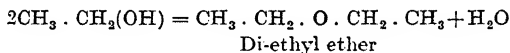
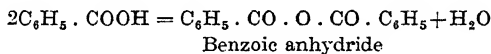
The above-mentioned examples all refer to combination between carbon atoms.

The following are typical condensations in the wider sense—

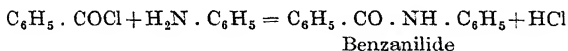
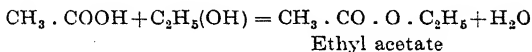
(d) Intramolecular condensation in the wider sense, for example:



(e) Extramolecular condensations in the wider sense, between like molecules, "autocondensation":



(f) Extramolecular condensation in the wider sense between unlike molecules:



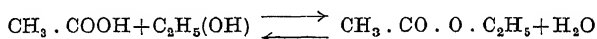
Thus, "condensation in the wider sense" includes those processes ordinarily described as etherification, lactone formation, anhydride formation, esterification, oximation, acetylation, and so forth.

Condensations take place with varying degrees of facility. In some cases the components react very energetically and the process takes place more or less spontaneously, when it is known as autocondensation. A reduction of temperature has a retarding effect, whilst temperature rise accelerates the reaction, which can be further regulated by the use of solvents, by which means the mixture is diluted and the temperature rise reduced in the case of exothermic processes. The degree

of temperature rise can be varied within wide limits by merely warming, boiling, melting, dry distillation, passage through heated tubes, and so forth. The application of pressure may also offer advantages.

In general, however, mere admixture of the reacting components is insufficient to initiate the reaction or to complete it within a reasonable time. There is frequently a tendency to the establishment of equilibrium, especially in the case of condensations in the wider sense, such as esterification, and so forth.

In some cases the reaction may be practically completed by continuously removing the volatile reaction product from the mixture by distillation. If, for example, in the reaction



the ethyl acetate is continuously removed, which is possible within certain limits, further formation of the ester occurs, beyond the limits imposed by the initial condition of equilibrium. This procedure alone is, however, generally insufficient, and it is usually better to use it in association with the fixation of the water by suitable reagents.

The circumstances are particularly favourable when the original equilibrium is continuously destroyed by internal transformation of the original product of reaction. An example of such a case is the formation of acetals from phenols with aldehydes, which shows no tendency to completion of the simple etherification process, but which is easily carried to practical completion owing to the further conversion of the acetal into a dihydroxydiphenyl-alkylide (or arylide):



This case also shows how nuclear condensations sometimes only occur after a preceding condensation in the wider sense.

**Condensing Agents.** By far the greater number of condensation processes require promotion, not merely by heating, but

by the additional presence of condensing agents, contact agents, or catalysts, a large number of which have been investigated. It may be broadly said that the action of all these agents is specific, as the choice of condensing agent must be made in accordance with the character of the liberated by-product ( $\text{H}_2\text{O}$ ,  $\text{HCl}$ , and so forth). The effect of these reagents has been only partially explained. In many cases additive compounds are formed between one of the reacting components and the condensing agent, which then interact with the other component of the mixture. In other cases, the action must be ascribed to a definite tendency for the fixation of the liberated by-products (fixation of water, hydrogen halide, and so forth). In other cases the action appears to be purely catalytic.

The following condensing agents have been found suitable in various cases—

1. Condensing agents when *water* is liberated: Inorganic and organic bases, salts of basic, neutral, and acid character; anhydrous salts, such as alkali acetates and the chlorides of aluminium, iron, magnesium and zinc; tin chloride, inorganic and organic anhydrous salts, acid anhydrides, the chlorides of phosphorus, and so forth.

2. Condensing agents when *halogen hydrides* are liberated: Alkalies, pyridine, carbonates and oxides, metals, aluminium chloride, zinc chloride, ferric chloride, and so forth.

3. Condensing agents when *hydrogen sulphide* is liberated: Bases, halogens, halides, carbonates, oxides, and so forth.

4. Condensing agents when *hydrogen* is liberated: Oxidizing agents of all kinds, such as air, permanganate, ferric chloride, potassium ferricyanide, oxides and superoxides, and so forth.

This summary is in no way exhaustive, but merely indicates those reagents ordinarily used.

It may be mentioned that the success of condensation experiments depends greatly on the character and quantity of the condensing agent which is used, the right selection of the character and quantity of which offers great difficulties and must be established from case to case by experiment. In the case of autocondensations, special attention must be directed to precautions against excessive temperature rise, as processes

which are otherwise sluggish may assume a violent character in presence of condensing agents. As a residue of excessive amounts of condensing agent is obviously undesirable in the reaction product, and may be difficult to remove, for technical purposes the minimum quantity is always used which suffices for sufficiently rapid operation. At the same time, in the special case of resin-forming condensation, attention must be directed to the production of mixtures, in accordance with the principles already referred to, and the processes must be chosen and carried out in accordance with this object.

Reaction products of resinous character may be expected, if:

- (a) The reaction product primarily produced is of unstable character, and is, more particularly, capable of a certain degree of polymerization;
- (b) if isomers are formed;
- (c) if chain-compounds are formed.

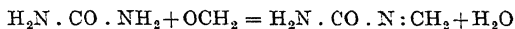
The case (a) is implied by a resin-forming condensation, as this is essentially carried out for the purpose of producing a complex which is capable of polymerization. It is, however, difficult to distinguish in such cases between resin-forming condensation and polymerization, as primary resins are often produced, which in practice, at least, must be described as condensation resins, and which are merely further transformed by polymerization. Such reactions cannot be classified under resin-forming polymerizations, as uncertainty often exists regarding the nature of the polymerizable constituents, and any views on the nature of the reaction are entirely speculative.

Where the resinous products are permanently soluble and fusible, the presumable polymerization reactions which follow the condensation are of minor importance only in their effect on the special properties of the resin. It is possible that they may exercise a decisive effect on the production of the necessary "typical mixture," but the importance of such polymerization processes is confined to the production of disuniformity in the reaction product. The conditions differ entirely if the resinous products possess the property of "hardening," that is, of being convertible by simple means from the soluble

and fusible condition into another of more or less definitely colloidal character, which may be practically indicated by loss of solubility and fusibility. In this case, the polymerizable resin-like products obtained by condensation, possess the property of potential complete alteration of their original character. This is of the greatest technical importance, for which reason resin-forming condensations which lead to such far-reaching polymerizations, constitute the most important methods of synthetic resin production.

As examples of simple resin formation by combined condensation and polymerization, we may refer to the work of W. Herzog and J. Kreidl<sup>1</sup> on resin production from benzal- and dibenzal-acetones, which have already been referred to when considering resin-forming polymerization. (See pages 107 *et seq.*) All the products produced by them possess permanent solubility and fusibility, and the polymerides which they contain are presumably never of greater complexity than dimerides, which act as practically inert constituents.

On the other hand, extremely active products are obtained by the reaction between urea and formaldehyde, probably according to the following equation—



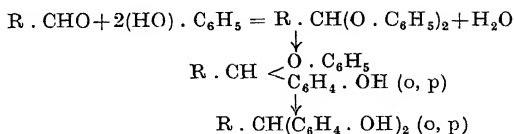
It is not surprising that in this case transformation proceeds until a completely insoluble and infusible glass-like mass is obtained, which is known as Polloplas.

Case (b) occurs, for example, if condensation in the wider sense first occurs, and is followed by transformations into substances produced by nuclear condensation. In such cases the reaction product is frequently a mixture of primary and secondary products, in which the resinous condition may be more particularly expected if the transformations lead to the production of isomeric products, such as positional isomers. As an example we will refer to the reaction between phenols and aldehydes, which first leads to the formation of acetals, which

<sup>1</sup> See more especially, *Angew.*, 35, 466 (1922).

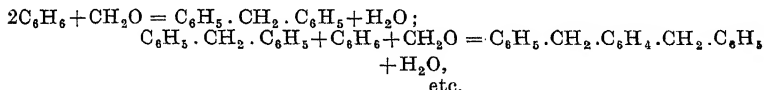


may then be transformed into semi-acetals, and ultimately into diphenylmethane derivatives:



The resin would in this case be a mixture of acetal, semi-acetal and diphenylmethane derivative. The complexity of composition is naturally very considerably increased if, in place of a single phenol, a mixture is used, for example, the technically available mixture of the three isomeric cresols, known as technical carbolic acid.

Chain-forming reactions (c) occur, for example, if aromatic hydrocarbons are caused to interact with formaldehyde, in which case diphenylmethanes are first produced, which then interact further with formaldehyde, in the same manner as the original hydrocarbons. As this series of reactions may be repeated still further and, in addition, the number of isomers rapidly increases, it is not surprising that the product is of resinous character if the reaction is suitably conducted. The reactions occur according to the following equations—



It is not in any way surprising that these various reactions may occur simultaneously. The more complicated the course of the reaction, the more certainly will the required resin-like condition be attained in the final product.

In a systematic discussion of resin-forming condensations, a subdivision on the basis of the principal reactions, namely, condensation with subsequent polymerization, formation of isomeric mixtures, chain-forming reactions, and so forth, would be impracticable, as no clear view could thus be obtained of the extremely numerous individual processes. It is better to

adhere to technical practice, and to name the various synthetic resins according to the raw materials employed, as phenol-formaldehyde condensation products, glycerine-phthallic acid resins, and so forth, thus basing our classification on the various reaction mixtures, and further to distinguish main groups, according to similarity of the evolved by-products.

Thus the processes of resin-forming condensation would be divided as follows—

1. Condensations in which water is liberated.
2. Condensations in which halogen hydrides are liberated.
3. Condensations in which hydrogen sulphide and so forth are liberated.
4. Condensations in which hydrogen is liberated (oxidations).
5. Various other resin-forming condensations.

**Condensations in which Water is Liberated.** These condensations are particularly important for the production of synthetic resins, as they include the greatest number of available processes and, because on account of the absence of acid, poisonous or evil-smelling by-products, such as hydrochloric acid or hydrogen sulphide, they enable neutral products to be obtained in an easy and convenient manner.

The number of possible reaction mixtures is extremely large. Formaldehyde (or its equivalents, trioxymethylene, polyoxymethylene, hexamethylene-tetramine, anhydroformaldehyde-aniline, methylene dichloride, and so forth) is an essential constituent in many cases, for which reason it may suitably be discussed first as a component of the reaction. The various reactions may then be classified as follows—

1. Condensates with *formaldehyde*:
  - (1) Phenol-formaldehyde products.
  - (2) Amine-formaldehyde products.
  - (3) Urea-formaldehyde products.
  - (4) Ketone-formaldehyde products.
  - (5) Hydrocarbon-formaldehyde products.
  - (6) Products from various other substances with formaldehyde.

2. Condensates with *aldehydes* other than formaldehyde and with ketones:

- (1) Phenol-aldehyde and phenol-ketone products.
- (2) Aldehyde and ketone condensates.
- (3) Condensates from aldehydes with ketones.
- (4) Condensates from aldehydes with amines or ammonia.
- (5) Condensates from amines and hydrocarbons.

3. Condensates with *alcohols*:

- (1) Condensates from alcohols with phenols.
- (2) Condensates from polyalcohols with polyatomic acids.
- (3) Other condensates from alcohols.

4. Condensations with *acids*.

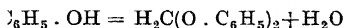
**Condensates with Formaldehyde.** Formaldehyde not only reacts as an aldehyde,  $\text{H} \cdot \text{CHO}$ , but also as methylene glycol,  $\text{CH}_2(\text{OH})_2$ .<sup>1</sup> In consequence of its very exceptional reactivity, it easily reacts with an extremely large number of representatives of many classes of substances, forming not only nuclear condensation products, but also many other condensation products in the wider sense, such as ethers, and so forth. These latter are frequently subject to further transformations, so that by carrying out the reaction suitably, a mixture of products with the characteristics of a resin may almost always be relied on as a product. In addition, the group  $\text{CH}_2 : \text{C} <$  is easily formed, and when suitably substituted shows a definite tendency to the formation of polymers. It is, therefore, not surprising that in numerous cases formaldehyde condensation products should take the form of resins which show a pronounced tendency towards conversion into "end" products. These various properties render formaldehyde or its equivalents an irreplaceable raw material for the production of synthetic resins.

**Phenol-formaldehyde Condensation Products.**<sup>2</sup> The reaction

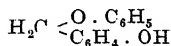
<sup>1</sup> See the work of Tollens and pupils, for example, *Ann.*, 265, 316 (1891); 276, 82 (1893); 289, 36, 46 (1896); *Ber.*, 36, 1341 (1903).

<sup>2</sup> The following general articles on phenol-formaldehyde condensation products may be referred to: L. H. Baekeland, *Chem. Ztg.* (1909), 317, 326, 347, 358, 1268; (1912), 1245; H. Lebach, *Angew.*, 22, 1598 (1909); *Chem.-Ztg.* (1913), 733, 750; Ullmann, *Encyclopaedia*, II, 129; VII, 297; Bottler, *Kunstharze*, Munich (1919); C. Ellis, *Synthetic Resins and Their Plastics*, New York (1923).

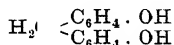
between formaldehyde and phenols corresponds to that between aldehydes and phenols in general (page 177 *et seq.*), and may be formulated as follows, in the case of ordinary phenol,  $C_6H_5 \cdot OH$ :—



It is not to be expected that the isolation of this diphenyl ether of dihydroxymethane should be possible under the conditions of the reaction, namely, in presence of acid. The product melts at  $18^\circ C.$  and is, therefore, liquid at the ordinary temperature,<sup>1</sup> and, moreover, it is generally found that acetals of this character are converted on heating in the presence of acids into methylene diphenols, a semi-acetal being formed as an intermediate product.<sup>2</sup> (See page 178.) In the case under consideration the following compounds might therefore occur—  
Semi-acetals,



and methylene-diphenols,



The presence of these latter compounds has actually been demonstrated. Thus, for example, A. W. Coster van Voorhout<sup>3</sup> succeeded in isolating p-dihydroxydiphenylmethane (melting point  $160.2^\circ C.$ ).<sup>4</sup> Subsequently, Trautenberg succeeded in

<sup>1</sup> C. A. Bischoff and E. Fröhlich, *Ber.*, 40, 2789 (1907). This includes a bibliography.

<sup>2</sup> See L. Claisen, *Ann.*, 237, 264 (1887); *Ber.*, 19, 3317 (1886). The reaction between formaldehyde and aniline proceeds quite similarly. Thus, according to C. Eberhardt and A. Welter, *Ber.*, 27, 1804 (1894), methylenediphenylimide,  $CH_2 \cdot (NH \cdot C_6H_5)_2$ , is first formed, analogous to acetal,  $CH_2 \cdot (O \cdot C_6H_5)_2$ . The transformation of the latter into methylenediphenol,  $CH_2 \cdot (C_6H_4 \cdot OH)_2$ , is analogous to the conversion of methylene-diphenylimide into diaminodiphenylmethane,  $CH_2 \cdot (C_6H_4 \cdot NH_2)_2$ , which also occurs under the influence of acids. See page 196 *et seq.*

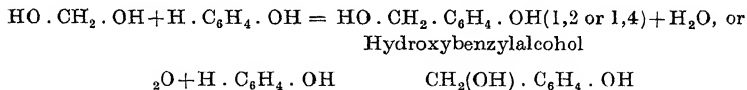
<sup>3</sup> *Chem. Weekblad*, 17, 2 (1920); *C.* (1920), II, 340.

<sup>4</sup> For the product obtained by melting the corresponding diphenylmethane disulphonic acid with caustic alkali the m.p.  $158^\circ C.$  has been found; see Beck, *Ann.*, 194, 318 (1874). C. Eberhardt and A. Welter, *Ber.*, 27, 1814 (1894), who obtained the same compound by diazotizing the diamino-compound, do not give the melting point.

isolating an isomeric product of melting point  $115^{\circ}\text{C}.$ ,<sup>1</sup> which may very probably be the o-p-product.<sup>2</sup> There is, therefore, no doubt that formaldehyde can enter into essentially the same reactions with phenols as other aldehydes. This is also shown by the work of N. Caro<sup>3</sup> and L. Kahl,<sup>4</sup> in which the methylene-diphenol derivatives obtained from formaldehyde and resorcin, pyrogallol, naphthoresorcin, salicylic acid and o-cresotic acid are described.

Although the formation of the methylene-diphenols is promoted by acid conditions in the mixture, the reaction can also occur in the presence of alkali or substances of similar chemical character. This was already shown for aldehydes,  $\text{R} \cdot \text{CHO}$ , by A. Michael.<sup>5</sup> That it also applies to formaldehyde is shown by the ease with which dihydroxydinaphthylmethane is formed on allowing an alkaline solution of formaldehyde and  $\beta$ -naphthol to stand,<sup>6</sup> and also by a statement of Auwers<sup>7</sup> that by the action of very strong caustic soda solutions not only are phenol alcohols formed, but also a certain proportion of dihydroxydiphenylmethanes.

It is true that under alkaline conditions another reaction, which is typical for formaldehyde, takes place by preference, namely, the formation of phenol-alcohols of the o- and p-series, as was shown independently by both L. Lederer<sup>8</sup> and O. Manasse.<sup>9</sup> The reaction may be considered either as a condensation or as an additive reaction (aldol formation), and takes place according to the following equations—



<sup>1</sup> *Angew.*, 36, 515 (1923).

<sup>2</sup> According to V. Wagner, *Journ. prakt. Chem.* (2) 65, 312 (1902), the melting point of this substance is  $117\text{--}118^{\circ}\text{C}$ . All the other known isomers, with the exception of the di-p-compound, melt at much lower temperatures.

<sup>3</sup> *Ber.*, 25, 947 (1892).

<sup>4</sup> *Ber.*, 31, 143 (1898).

<sup>5</sup> *Ber.*, 17 R, 21 (1884).

<sup>6</sup> O. Manasse, *Ber.*, 27, 2412 (1894).

<sup>7</sup> *Ber.*, 40, 2525 (1907).

<sup>8</sup> *Journ. prakt. Chem.* (2), 50, 223 (1894).

<sup>9</sup> *Ber.*, 27, 2409 (1894); German Pat. 85,588 (Bayer & Co.).

By using larger quantities of formaldehyde than correspond to the molecular ratio 1 : 1, more than one primary  $-\text{CH}_2 \cdot \text{OH}$  group can be introduced.<sup>1</sup> On heating, such polyvalent alcohols easily liberate formaldehyde, whilst the hydroxybenzyl alcohols manifest a similar tendency on much more energetic treatment only.<sup>2</sup> The considerable tendency to form phenol-alcohols in presence of alkaline agents is shown by the fact that the proportion of phenol in excess of one molecule may be simply distilled off.<sup>3</sup> It is interesting to note, in this connection, that hydroxybenzyl alcohol has also been found in the product obtained under acid conditions,<sup>4</sup> although its detection is difficult owing to the ready resinification of phenol-alcohols, due to the formation of anhydrides (Saliretenes) referred to below.

Either form of interaction of formaldehyde with phenols leads with equal facility to mixtures of resinoid character. As, broadly speaking, acid condensing agents, such as acids and salts showing an acid reaction on hydrolysis, cause interaction between 2 molecules phenol and 1 molecule formaldehyde, whilst basic condensing agents, such as bases and substances of equivalent action, more especially salts which give a basic reaction on hydrolysis, cause interaction between 1 molecule phenol and 1 molecule formaldehyde, two main classes of phenol-formaldehyde condensation products can be distinguished. This distinction is by no means merely theoretical, as the products condensed in an acid medium are permanently soluble and fusible, whilst those condensed in a basic medium are all readily converted into insoluble and infusible products.

The reason for this distinction is to be found in the differing constitution of the two classes of resin. The products of acid condensation are mixtures of acetals, semi-acetals and methylene-diphenols, containing some unchanged phenol or dissociation products of the condensates.<sup>5</sup> The products

<sup>1</sup> Chem. Fabriken, Dr. K. Albert, G. m. b. H., U.S. Pat. 1,614,171; British Pat. 261,472; French Pat. 596,072; *C.* (1927), I, 1890

<sup>2</sup> F. Raschig, *Angew.*, 25, 1946 (1912), Note 2.

<sup>3</sup> H. Lebach, *Chem.-Ztg.*, (1913), 734.

<sup>4</sup> L. H. Baekeland, *Chem.-Ztg.*, (1912), 1246.

<sup>5</sup> A. Dianin, *Ber.*, 25 R. 334 (1892).

obtained under alkaline conditions, on the other hand, must be considered essentially as mixtures of various phenol-alcohols, which also, of course, contain a certain proportion of unchanged phenols.

As the special technological importance of the two classes of resins, arising out of the above differences, will be discussed in a special chapter, we need only refer here to the special nomenclature which has been introduced for these various products, and for their various transformation stages.

**Nomenclature.** The products of acid condensation, which are, practically speaking, permanently soluble and fusible,<sup>1</sup> are known as Shellac substitutes, or as Novolak.<sup>2</sup> The so-called Saliretines should also be included in this class.

The products of basic condensation, which can be further transformed by simple heating, are known as Resoles<sup>3</sup> or Initial condensates,<sup>4</sup> when in liquid form, or in soluble and fusible solid form. After conversion into hard, heat-resistant, insoluble and infusible masses, they are known as Resites or Final condensates, for which the term Phenoplast has recently been suggested.<sup>5</sup> An intermediate stage may be distinguished, which it was formerly customary to call the Intermediate condensate or Resitol.<sup>6, 7, and 8.</sup>

The question of most scientific interest is undoubtedly that of the nature of the hardening transformation.

The conditions are very complicated, as pure substances are not present. However, sufficient data are available to indicate the main character of the reactions which occur. The following has been established—

1. Chemically pure o- and p-hydroxybenzyl alcohols can be

<sup>1</sup> On prolonged heating to a high temperature partial hardening occurs; see L. H. Baekeland, *Chem. Ztg.* (1912), 1246.

<sup>2</sup> L. H. Baekeland, *Chem.-Ztg.* (1909), 858.

<sup>3</sup> H. Lebach, *Angew.*, 22, 1601 (1909).

<sup>4</sup> L. H. Baekeland, British Pat. 1921 (1908); U.S. Pat. 942,809.

<sup>5</sup> O. Gamber, *Drechselbare Kunstharze*, Hartlebens Bibl. No. 381 (1926).

<sup>6</sup> German Pat. 237,790.

<sup>7</sup> H. Lebach, *Chem.-Ztg.* (1913), 734.

<sup>8</sup> The Bakelite-Gesellschaft m.b.H., Erkner-Berlin, uses the registered name "Bakelite," to which it adds "A," "B," or "C" to designate the various stages of treatment.

converted into typical resites by sufficiently prolonged heating to a high temperature.<sup>1</sup>

2. Mixtures of phenol-alcohols undergo the same change much more easily and rapidly.<sup>2</sup>

3. Dihydroxydiphenylmethanes are not convertible into Resites.

4. In alkaline condensations, even in the presence of a large amount of alkali (KOH), the reaction between phenol and formaldehyde proceeds as far as resite formation, even at water-bath temperature.<sup>3</sup>

5. Novolak is converted into resite by treatment with formaldehyde in the absence or presence of contact agents (bases or acids).<sup>4</sup>

6. Resol is spontaneously transformed into resite under the influence of acids.<sup>5</sup>

7. All the indications point definitely to the nature of the transformation as a polymerization process, in the course of which a hemi-colloid is formed. In particular, the intermediate product, Resitol, must be considered to be an analogue of "vitreous styrol,"<sup>6</sup> that is, a solid solution of Resite in Resol.<sup>7</sup>

8. In order to achieve maximum hardness, the addition of formaldehyde is necessary or advantageous.

The study of the phenol-alcohols, and more especially of saligenin (o-hydroxybenzyl alcohol) has shown that under the influence of acids they undergo a very considerable transformation into anhydrides of ethereal character, which form resins, known as Saliretins.<sup>8</sup> This reaction is quite comprehensible, as chain formation can theoretically involve an indefinite

<sup>1</sup> F. Raschig, *Angew.*, 25, 1946 (1912).

<sup>2</sup> *Loc. cit.*; see also German Pat. 189,262; de Laire.

<sup>3</sup> German Pat. 157,553; Henschke.

<sup>4</sup> H. Lebach, *Chem.-Ztg.* (1913), 736; Aylsworth, British Pat. 3,498 (1911).

<sup>5</sup> See British Pats. 27,096 (1908); 6,430 (1911); Knoll & Co.

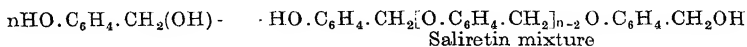
<sup>6</sup> H. Stobbe and G. Posnjak, *Ann.*, 371, 259 (1909).

<sup>7</sup> See also L. H. Baekeland and H. L. Bender, *Kunstst.* (1925), 216.

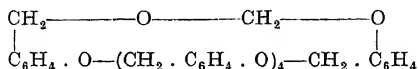
<sup>8</sup> Piria, *Ann.*, 56, 39 (1845); *Ann. chim. phys.* (3), 14, 268 (1845); Beilstein and Seelheim, *Ann.*, 117, 84 (1861). The last two authors also found that saligenin is converted into an insoluble product on heating with  $\text{PCl}_5$  in a sealed tube. A similar product was obtained by C. Paal and Senninger, *Ber.*, 27, 1802 (1894), by treating saligenin in a sealed tube with alcoholic ammonia, and was named Saliretazin. A similar result was obtained by L. K. Baekeland, *Chem.-Ztg.*, 33, 857, by heating with phenol under pressure.



number of molecules, so that all the conditions are present for the formation of mixtures, the individual components of which are mutually soluble—



As L. H. Baekeland was able to show that this chain-formation can also be effected by heating, and that the best production of resite is obtained by the interaction of 6 molecules of phenol-alcohol with 1 molecule of formaldehyde, he concluded that the final product was built up from the component molecules as follows :<sup>1</sup>



that is, that it consisted of hexa-hydroxybenzyl-methylene-glycol anhydride complexes.

This conclusion is, however, hardly in accordance with the actual behaviour of resites, although it may be admitted that the presumable internal ring tension might suffice for the formation of association colloids. (See pages 54 and 76.) But the extremely slight tendency to transformation of phenol-alcohols in a basic medium<sup>2</sup> makes it scarcely possible that resite formation should be a reaction similar to the saliretine reaction, in view of the facts referred to under 4 above.

A similar objection holds to the theory of resite formation recently formulated by H. Barthélemy,<sup>3</sup> who considers the cause for the formation of colloidal complexes to be the far-reaching capacity for chain formation of the phenol-alcohols. It could be shown by cataphoretic tests that products of that kind are formed, for whilst the colloids obtained in an alkaline medium migrated to the cathode, those obtained in an acid medium migrated to the anode. Barthélemy considers that this proves the occurrence of two essentially different classes

<sup>1</sup> *Chem.-Ztg.* (1909), 358; Ger. pat. 189,262.

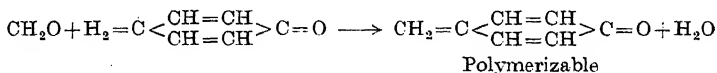
<sup>2</sup> The method of preparing phenol-alcohols according to L. Lederer or O. Manasse is directly based on the stability of these products to alkali.

<sup>3</sup> *Kunstst.* (1925), 150; *La Revue des Produits Chim.*, 28, 361 (1925).

of phenol-formaldehyde condensation products, which he formulates as follows—

1.  $\left[ \left( \sum_1^n \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \right) \text{H} \right] \text{OK}$       Product obtained with alkali.
2.  $\left[ \left( \sum_1^n \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{CH}_2 \right) \text{H} \right] \text{Cl}$       Product obtained with acid.

A. Wohl and B. Mylo<sup>1</sup> make the interesting suggestion that the resites may be polymerized methylene-phenols, derived from the tautomeric form of the phenols. It is, however, difficult to explain the formation of complexes of such a character, although their powers of polymerization, if formed, would be beyond question; for the ease with which resites are formed in a strongly alkaline solution (see 4, page 147) shows that it is very unlikely that the reaction could occur as follows—



as the presence of alkali would prevent the formation of the ketonic form of phenol. Attempts to explain the formation of such polymerizable substances in any other way appear very doubtful.<sup>2</sup>

F. Raschig<sup>3</sup> attempted to explain the basis of resite formation in quite another manner. Starting from the fact of the smooth and easy conversion of mixtures of phenol-alcohols into resites, and the further fact that products which are stable to alkali are formed with especial ease in the presence of excess of formaldehyde, he suggested the following course of the reactions.

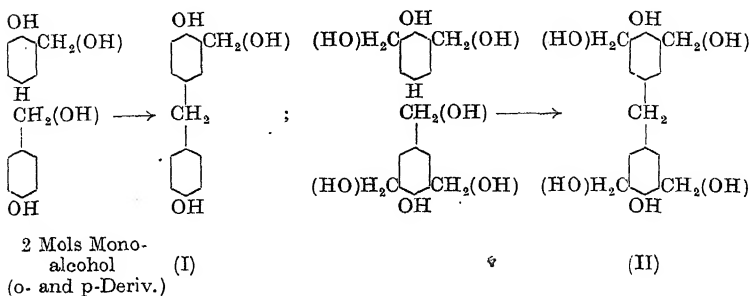
The isomeric phenol-alcohols first interact to form dihydroxydiphenylmethane derivatives. In the case of monovalent

<sup>1</sup> *Ber.*, 45, 2046 (1912), Note 1.

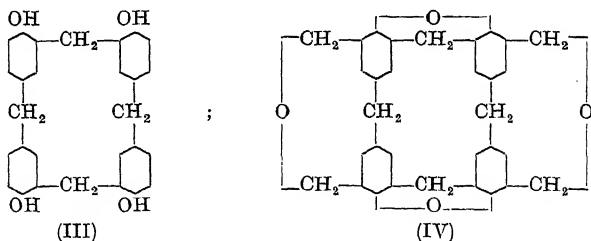
<sup>2</sup> One might assume a reaction similar to that which occurs during the conversion of methylenediphenylimide,  $\text{CH}_2 \cdot (\text{NH} \cdot \text{C}_6\text{H}_5)_2$ , into anhydroformaldehyde-aniline,  $\text{CH}_2 : \text{N} \cdot \text{C}_6\text{H}_5$ ; see C. Eberhardt and A. Welter, *Ber.*, 27, 1805 (1894).

<sup>3</sup> *Angew.*, 25, 1946 (1912).

alcohols, this leads to the formation of complexes such as (I), whilst polyvalent alcohols form complexes such as (II).



Two molecules of these dihydroxymethane-alcohols then condense further to form more complicated molecules of the types (III) or (IV), thus producing products which are either soluble in alkali, or insoluble in consequence of the formation of internal anhydrides. The production of the latter assumes the interaction of a certain further quantity of formaldehyde.



These views have recently been again adopted by W. Herzog and J. Kreidl,<sup>1</sup> as by a simple re-arrangement of formulae such as (IV), the presence of resinophoric groups can be indicated, which can be used to explain the production of further higher polymers. It must, however, be stated that these assumptions appear scarcely adequate in this particular case.

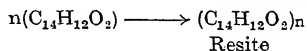
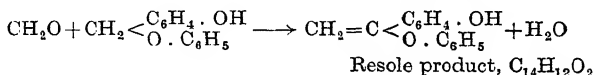
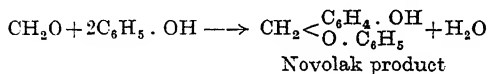
The fact must be taken into account that a complex of very great polymerizing capacity must be formed in the earliest

<sup>1</sup> *Angew.*, 35, 643 (1922).

phase of the reaction. As the suggestions of Barthélemy and of Wohl and Mylo, which would in any case be very speculative, may be dismissed, owing to the facility with which resites are formed in strongly alkaline solution, the most probable remaining assumption is that recently propounded by L. H. Baekeland and L. H. Bender,<sup>1</sup> who start from the fact that dihydroxydiphenylmethane derivatives have been detected with certainty as intermediate products. If these substances are treated with formaldehyde, methylene derivatives are formed as follows—



to which a tendency to polymerization may be attributed. Baekeland and Bender, therefore, formulate the formation of the Novolak resins and resole products in the following manner—



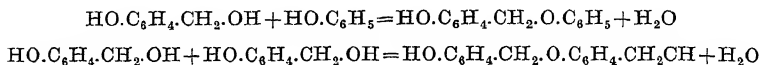
This view has undoubtedly the advantage of great simplicity, and also explains the various circumstances of the case. The assumption of the formation of semi-acetals in Novolak products is inessential, as obviously acetal itself and methylenediphenol would represent absolute equivalents, the formation of which would depend on the conditions of the experiment. (See below.)

In the first instance, it explains how Novolak products are converted into resites by treatment with formaldehyde. It also explains quite satisfactorily why the products so obtained are in no way inferior to those obtained directly from resoles.

An explanation of the formation of resoles in alkaline media

<sup>1</sup> *Kunstst.* (1925), 216; *Ind. and Engin. Chem.*, 17, 225 (1925); *C.* (1925), I, 2729.

is, perhaps, more difficult, as in this case phenol-alcohols are undoubtedly present. It should, however, be remembered that Raschig's view that phenol-alcohols are able to interact with phenol, or even with other molecules of phenol-alcohol,<sup>1</sup> is strongly supported by von Auwers' observation of the formation of dihydroxydiphenylmethane in alkaline solution. These interactions would first lead to the semi-acetal or phenol-alcohol of such a substance.



In the usual charges, which contain 1 molecule of formaldehyde for each molecule of phenol, the simple semi-acetal would first react directly with formaldehyde, thus forming the polymerizable complex. In the case of the phenol-alcohol of the semi-acetal this would, however, only be possible in so far as further formaldehyde were available, as in that case the monomolecular proportion has already been disposed of. To the extent, therefore, to which the phenol-alcohol of the semi-acetal is produced, non-polymerizable molecules will accumulate in the resin mixture, the practical effect of which will be manifested by retardation of the further transformation process. As the primary alcohol group is gradually eliminated in the form of formaldehyde on heating, the capacity of the product for being hardened still remains, but is considerably accelerated by the further addition of formaldehyde. As in this manner the completion of the reaction is most certainly secured, the advantage of this procedure is fully explained.

The fact, which is on the face of it somewhat surprising, that mixtures of various phenol-alcohols interact far more easily than chemically pure individuals, may be simply connected with the varying degrees of reactivity of the individual phenol-alcohols; for one isomer will unquestionably form ethers more easily than others, whilst another perhaps shows a greater tendency to liberate the primary alcoholic group in the form

<sup>1</sup> *Angew.*, 25, 1945 (1912); the author formulates the process as a nuclear condensation, which is improbable.

of formaldehyde. Such assumptions, which may certainly be applied to the o- or p-hydroxybenzylalcohols, would explain the smooth interaction of both isomers and the comparative inertness of the chemical individuals alone.

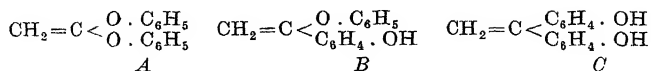
Whilst the formation of resole resins in alkaline media is largely independent of the proportions of the interacting raw materials, resoless are only formed under acid conditions if the components are present in at least molecular proportions and also after prolonged heating only. This shows that the interaction of the formaldehyde with the actual acetal, which must be assumed to be the primary complex, takes place with difficulty if at all. As the conversion into semi-acetal or methylenediphenol requires time, this explains the necessity for the prolonged duration of the reaction, on which the concentration or acidity of the condensing agent is also of influence. When preparing finished Novolak, the transformation is effected during the so-called "concentration" of the batch, with the object of attaining a product of the highest possible melting point.<sup>1</sup> Therefore the admixture of formaldehyde or trioxymethylene to such "finished" resin may act directly by the production of polymerizable complexes.

The essential difference, therefore, between basic and acid condensing agents depends on the fact that with the former the formation of the acetal stage is avoided, the semi-acetals being at once formed. With acid condensing agents, on the contrary, the acetal is first produced, and its further transformation requires some time. After the attainment of this stage, the difference in the action of the two classes of reagents disappears. More particularly with regard to the development of the polymerizable complexes themselves, and their further polymerization, it is immaterial whether basic or acid reagents are used.

It is difficult to form a definite opinion with regard to the exact structure of the polymerizable complexes. The assumption of the formation of the semi-acetal is arbitrary, although

<sup>1</sup> It should be remembered that methylenediphenolether (the acetal) melts at 18° C., whilst p-p-dihydroxydiphenylmethane melts at 160° C. and the o-p-derivative at 115° C. (117°-118° C.).

very probable, as already explained. Of the most obvious possibilities.



*C* is presumably not polymerizable, as already explained (page 97), or at any rate not to any important degree. This objection applies to neither *A* nor *B*. It should, however, be noted that a resite (*B*)<sub>n</sub> would be sensitive to alkalis, whilst, although (*A*)<sub>n</sub> would be insensitive to alkalis,<sup>1</sup> it would not explain the ready formation of resite in an alkaline medium. It is, of course, possible that equilibria are established in the melt between *A*, *B*, and *C*, which alter continuously in the direction of the most readily polymerizable substance. In this way the predominant formation of (*A*)<sub>n</sub> could be explained, which would further explain the resistance of the polymerized system to alkali. The circumstance must, however, be taken into account, that by the dry distillation of carefully prepared resite products, about 20 per cent only of phenol can be separated,<sup>2</sup> which fact is not in satisfactory accordance with the existence of a polymerized acetal. It might, therefore, be advisable to consider the possibility of tautomerization, which might, of course, lead to premature formation of product *C*. It should certainly be remembered that insolubility in alkali might be caused by transformation of *p*- into *o*-derivatives, followed by anhydride formation.<sup>3</sup>

In the latter case, the possibility must be allowed for that by the linkage of the two phenyl groups which are unsymmetrically united to the methylene group, a substance of similar constitution to diphenylethylene might be formed (see page 95), which would result in considerable increase in the polymerizing capacity.

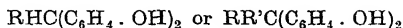
Thus, in spite of the undoubted advance which the theoretical views of resite formation have made, numerous questions

<sup>1</sup> Thus, according to A. Claus and E. Trainer, *Ber.*, 19, 3010 (1886), the substance  $\text{CH}_3 \cdot \text{CH}(\text{O} \cdot \text{C}_{10} \cdot \text{H}_7 - \beta)_2$  is unattacked by boiling alkali solution.

<sup>2</sup> W. Herzog, *Angew.*, 34, 97, 159; *C.* (1921), II, 1067; IV, 195.

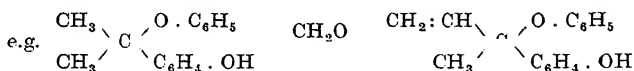
<sup>3</sup> L. Claisen, *Ann.*, 237, 264 (1887); *Ber.*, 19, 3317 (1886).

still remain unsettled. Resite formation cannot only occur from the direct reaction products of phenols with formaldehyde, but also from products of phenolic character which are obtained by the action of acetaldehyde or of methyl-ketones on phenols. The reactions in question, which occur in the presence of acid, lead to the formation of substituted methylenediphenols:



If these substances are treated with formaldehyde, resites are obtained by a smooth reaction.<sup>1</sup>

According to L. H. Baekeland and L. H. Bender, the action may be explained by the interaction of formaldehyde with one of the methyl groups:

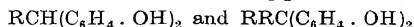


This applies to all methyl derivatives of the above character, and in the case of dimethyl compounds two molecules of formaldehyde may react. In all these cases compounds are formed of the general character,  $\text{CH}_2=\text{CH} \cdot \text{X}$ , where X represents a negative group, which may vary from case to case. In accordance with our earlier explanations, these constitute the best conditions for far-reaching polymerization to form resites.<sup>2</sup>

From the above it will be clear why, on replacing formaldehyde by other aldehydes, the capacity of the resins so formed to produce resites rapidly diminishes. With acetaldehyde the action is already very slight, whilst with propionic aldehyde or aromatic aldehydes it is non-existent. Furfural forms an exception, but in this case the constitutional factors are of another character.

<sup>1</sup> W. A. Beatty, U.S. Pat. 1,225,748.

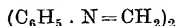
<sup>2</sup> It should also be borne in mind that, being phenols, the compounds



may interact with formaldehyde to form the corresponding phenol-alcohols. The products so obtained would show resole characters equally with the simpler products. In actual fact it is possible to "harden" any phenol-formaldehyde condensation product by treatment with formaldehyde, although with increasing molecular weight of the reacting complex, this becomes increasingly inert.



**Amine-formaldehyde Condensation Products.** In its interactions with amines, formaldehyde also takes up a special position amongst aldehydes. Thus, for example, with aniline, in acid or neutral solution, formaldehyde forms anhydroformaldehyde-aniline,



a crystalline product of polymeric character, which is convertible into a resin by heat, and so forth. (See page 126.) In alkaline alcoholic solution, aniline and formaldehyde produce methylenediphenyldi-imide,<sup>1</sup>

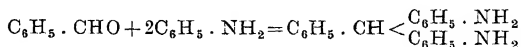


which, on heating on the water bath for about 12 hours with aniline and aniline hydrochloride, is converted into diamino-diphenylmethane,



a reaction which is accompanied by resin formation. Formaldehyde reacts similarly with other primary aromatic amines, condensation taking place by preference between the carbon and nitrogen atoms.<sup>2</sup>

On the other hand, the reaction between other aldehydes,  $\text{R} \cdot \text{CHO}$ , and primary aromatic amines, when the latter are present as sulphates, usually results in the linkage of carbon to carbon, for example,



In this reaction the p-position to the amino group is mainly occupied. If this is occupied reaction occurs with the hydrogen atom in the o-position. The reaction probably always occurs with intermediate formation of an aldol-like product, which has frequently been isolated and which reacts with a second

<sup>1</sup> Eberhardt, Welter, *Ber.*, 27, 1804 (1894).

<sup>2</sup> On the products of high molecular weight (e.g. M. 1,126-1,148) obtainable with o-toluidine, m-toluidine, and xylidine, with formaldehyde in sulphuric acid solution, see P. M. Kroneberg, *J. Russ. Phys. Chem. Ges.* 48, 305 (1916); *C.* (1924), I, 2422.

amine molecule, with liberation of water, to form the above products—

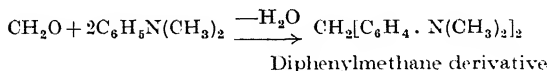
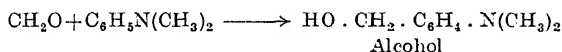
1.  $C_6H_5 \cdot CHO + C_6H_5 \cdot N(CH_3)_2 = C_6H_5 \cdot CH(OH) \cdot C_6H_4 \cdot N(CH_3)_2$
2.  $C_6H_5 \cdot CH(OH) \cdot C_6H_4 \cdot N(CH_3)_2 + C_6H_5 \cdot N(CH_3)_2 = C_6H_5 \cdot CH < \begin{smallmatrix} C_6H_4 \cdot N(CH_3)_2 \\ C_6H_4 \cdot N(CH_3)_2 \end{smallmatrix} + H$

The second phase occurs with increasing difficulty as the acidity of the liquid is increased.<sup>1</sup>

The course of the reaction with formaldehyde, on the other hand, appears to show more analogy with that with the aliphatic alcohols. With primary aromatic bases or their hydrochlorides these first form N-alkyl derivatives which are further transformed into nuclear homologues by migration of the alkyl group. For example,

1.  $C_6H_5 \cdot NH_2 \cdot HCl + CH_3 \cdot OH = C_6H_5 \cdot NH \cdot CH_3 \cdot HCl + H_2O$
2.  $C_6H_5 \cdot NH \cdot CH_3 \cdot HCl \rightleftharpoons \begin{smallmatrix} \sim \\ \sim \end{smallmatrix} NH_2 \cdot HCl$

With excess of formaldehyde in acid solution tertiary aromatic bases form alcohols, in which the alcohol residue occupies the p-position to the amino group, or the o-position if the other is occupied. With an excess of the base (2 molecules base to 1 molecule formaldehyde) diphenylmethane derivatives are formed—



Some of the above-described reactions have been proposed for the production of resins.<sup>2</sup> As will be realized, the many possibilities for interactions and transformations imply favourable conditions, as in many cases the production of mixtures can be relied on.<sup>3</sup> Böhler's resin, which is now considered as a polymerized product (see page 126), may owe its resinous

<sup>1</sup> Houben, *Die Methoden der org. Chemie*, Third Edition, Vol. II, pp. 898 *et seq.*

<sup>2</sup> See patent summary by Aladin, *Kunstst.*, 18, 36 (1928).

<sup>3</sup> On the reaction between p-toluidine and formaldehyde, see more especially C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, 123, 2745 (1923).

character largely to the occurrence of transformations, as is indicated by the fact that the addition of aniline exerts a favourable effect. The following amines have been recommended for the production of resins by interaction with formaldehyde—

*Aniline Hydrochloride.* The aqueous solutions of this substance yield plastic masses after adding formalin, cooling the product of the reaction, and again adding formalin.<sup>1</sup> According to more recent processes acetic acid is used. Improvements have also been made in the treatment of the primary product, such as heating in vacuo or under pressure; the latter process may be preceded by treatment with alkaline electrolytes.<sup>2</sup>

*Naphthylamines.* Mixtures of  $\alpha$ - and  $\beta$ -naphthylamine are caused to interact with formaldehyde; in order to improve the resistance to light, the above mixture of bases may be replaced by mixtures of  $\alpha$ -naphthylamine and primary amines of the benzene series.<sup>3</sup> The products resemble colophony.

*Resinates or Fatty Acid Salts of Aromatic Amines.* Mixtures of resin acids or higher fatty acids with aromatic amines (aniline) are condensed with formaldehyde. The resinous products are insoluble in water, soluble in alcohol, ether, acetone and chloroform. They are stated to be similar to shellac, but are insoluble in caustic alkali solution.<sup>4</sup>

<sup>1</sup> A. Allers, German Pat. 168,358; see also *Kunstst.*, I, 313 (1910). On the properties of a condensation product obtained by heating 1 molecule aniline hydrochloride with  $1\frac{1}{2}$  molecules formaldehyde in dilute aqueous solution, see German Pat. 406,218 (1923); *C.* (1925), I, 1658; the products, which are used for the manufacture of dyestuffs, are amorphous, pale yellow powders insoluble in chloroform, partially soluble in nitrobenzene, easily soluble in pyridine and soluble in glacial acetic acid with orange red colour, which decompose, without melting, at 130° C.

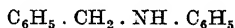
<sup>2</sup> L. Light, British Pat. 275,725; I. G. Farbenind. A.-G., German Pat. 452,009; La Fibre Diamond, British Pat. 282,435; P. Haller, Swiss Pat. 123,515; Ges. chem. Ind. Basle, British Pat. 283,965; see also I. G. Farbenindustrie A.-G., German Pat. 453,276; British Pat. 274,155; French Pat. 612,306; *C.* (1928), I, 2,463.

<sup>3</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 303,953 (1916) and 305,026 (1917); *C.* (1922), II, 879.

<sup>4</sup> L. Berend, German Pat. 222,512; see also *Kunstst.*, 2, 153 (1912); 2, 10, 173; *C.* (1910), II, 122. On a plastic mass from a fatty drying oil (Tung oil), formaldehyde and an amine, e.g. o-toluidine, see L. Lilienfeld, German Pat. 259,840 (1912); *Kunstst.*, 3, 257 (1913); Austrian Pat. 54,719; *Kunstst.*, 2, 393 (1912); U S Pat. 1,090,730; *Kunstst.*, 4, 275 (1914); German Pat. 246,443 (1910); *Kunstst.*, 2, 235 (1912).

*Methylaniline and Methyl diphenylamine.* On heating with formaldehyde and hydrochloric acid, resins are formed which have been recommended as copal substitutes and for the production of sealing-wax.<sup>1</sup>

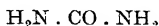
*Benzylaniline,*



When 9 parts of this substance are heated for 1 hour with 10 parts of 40 per cent formaldehyde, 20 parts of water and 1 part of hydrochloric acid, they yield a brittle, brownish yellow, transparent resin, soluble in the cold in benzene and in trichlorethylene and on heating with turpentine oil. Organic acids or alkalis are unsuitable as condensing agents. The resin which is produced is considered to be a diphenylmethane derivative.<sup>2</sup>

*Aliphatic Amines.* A resinous material, which is probably the polymer of an oily condensation product from aliphatic amines and formaldehyde, is obtained by the action of alkyl halides on hexamethylenetetramine.<sup>3</sup> The addition product which is first formed is hydrolysed, forming formaldehyde and alkylamine-halogen hydrates, condensed to trialkyltrimethylenetriaminehalogen hydrates, which are decomposed with alkali hydroxide, so obtaining the free bases, which are finally converted into resin by treatment with steam and distillation. Both the final products and the oily bases themselves are alleged to be used as accelerators for the vulcanization of rubber.

**Urea-formaldehyde Condensation Products.** Urea, or carbamide,



the diamide of carbonic acid, reacts with formaldehyde in many directions by which technically valuable products can be obtained, with elimination of water. By recent processes, water-clear, viscous solutions have been obtained as intermediate products, known as "Schellan" solutions, which are

<sup>1</sup> C. Goldschmidt, *Chem.-Ztg.* 29, 33, 444; *C.* (1905), I, 571, 1516.

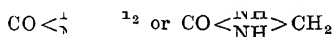
<sup>2</sup> Herzog, *Osterr. Chem.-Ztg.*, 24, 16, 28; *C.* (1921), II, 855; IV, 44.

<sup>3</sup> Naugatuck Chem. Company, M. G. Shepard, H. S. Adams, U.S. Pat. 1,471,213; British Pat. 207,499; Canadian Pat. 242,445; *C.* (1926), II, 2500; German Pat. 448,697; *C.* (1928), I, 2237.

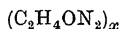
intended for use as adhesives. Further condensation leads to products such as "Pollopas," which is a glassy material of exceptionally valuable properties, and which represents an "aminoplast,"<sup>1</sup> which shows certain analogies to the "phenoplasts" or resites. Similar condensation products have been recommended for the production of varnishes, meerscham substitutes, and other plastic masses. These products have attracted so much interest that we have thought it advisable to devote a special section to their consideration in a later chapter; the fundamental reactions only will be discussed here.

The condensation between formaldehyde and urea is greatly influenced both by the character of the condensing agent,<sup>2</sup> and by the proportions in which the two ingredients are caused to interact.<sup>3</sup>

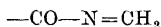
In acid solution (HCl), formaldehyde and urea, in the proportions of about 1 molecule and less of the former to 1 molecule of the latter, form methylene-urea:<sup>4</sup>



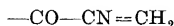
Methylene-urea, which must be considered to be a polymer,



is an amorphous powder, only slightly soluble in water, which is reconverted into formaldehyde and urea by mineral acids. The atomic configuration which must be assumed in methylene-urea,



is analogous to that found in the methylene-ketones,



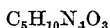
<sup>1</sup> This expression was coined by O. Manfred and J. Obrist, *Kolloidzeitschr.*, 42, 175 (1927). "Prystal" is another material similar to Pollopas; see H. Barthélemy, *Chimie et Industrie*, 16, 367 (1926).

<sup>2</sup> Goldschmidt, *Chem.-Ztg.*, 21, 460, 586 (1897).

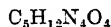
<sup>3</sup> Dixon, *Trans. Chem. Soc.*, 113, 238 (1918); M. van Laer, *C.* (1923), 1, 901.

<sup>4</sup> Lüdy, *Monatshefte f. Chem.* 10, 297 (1889); von Hemmelmeyer, *Monatshefte f. Chem.*, 12, 94 (1891); Thoms, *C.* (1897), II, 145, 737; Littirschaid, *Ann.*, 316, 180 (1901); Dixon, *loc. cit.*

which, as already mentioned, is characterized by exceptional polymerizing capacity (page 105). If an excess of formaldehyde is employed for the condensation in acid solution, a product is obtained of the composition



as a dense, white, granular precipitate,<sup>1</sup> which is completely insoluble, and is decomposed by strong acids, but unattacked by alkalis. According to Dixon,<sup>2</sup> this is the only product which is obtained if the proportion of formaldehyde is from 1.5 to slightly more than 2 molecules. Higher proportions of formaldehyde diminish the yield, which is already very small if 4 molecules are present. The product then obtained has the composition,



In the presence of 11 molecules no condensation occurs.

In the presence of barium hydroxide, Einhorn and Hamburger obtained crystalline mono- and di-methylolurea.<sup>3</sup>

A 37.4 per cent formaldehyde solution is allowed to drop into a solution of urea and barium hydroxide in water, with ice cooling, and as soon as the formaldehyde has completely disappeared carbon dioxide is led in, in order to remove the barium hydroxide. The isolated methylolurea,



is obtained from alcohol in prisms of melting point 111° C. It is easily soluble in water and in methyl alcohol, but insoluble in ether. On adding dilute acids or acetic acid an amorphous precipitate is immediately obtained.

*Dimethylolurea.*  $\text{CO}(\text{NH} \cdot \text{CH}_2 \cdot \text{OH})_2$ . This is obtained by

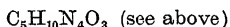
<sup>1</sup> Carl Goldschmidt, *Ber.*, 29, 2438 (1896); *C.*, (1897), II, 194, 736.

<sup>2</sup> *Loc. cit.*; C. Ellis, *Synthetic Resins*, p. 239 *et seq.*

<sup>3</sup> *Ber.*, 41, 27 (1908); *Ann.*, 361, 131 (1908); compare Beilstein, III, 59; see also Beilstein on condensation products of oily and of crystalline character from methylurethane and formaldehyde, and from urea, formaldehyde and large proportions of organic bases.

adding urea to a solution of barium hydroxide in 37.4 per cent formaldehyde solution at 25° C., and removing the barium hydroxide by passing in carbon dioxide as soon as all the formaldehyde has disappeared. The product crystallizes from absolute alcohol in prisms, and from dilute alcohol or water in small plates, sinters at 121° C., and melts at 126° C. to a liquid which resolidifies at 137–138° C. with liberation of water and formaldehyde, to form an amorphous substance which decomposes, without melting, at about 260° C.

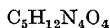
Dimethylolurea is fairly easily soluble in cold water, warm ethyl and methyl alcohols, but otherwise insoluble. On heating it in a test-tube, a smell of formaldehyde and of basic decomposition products can be observed. Tollens' silver solution is only reduced after some time. By the action of alkalis amorphous condensation products are produced. According to Dixon the compound,



is produced either by heating the product or by treating its solution with dilute hydrochloric acid.

In alkaline solution and in presence of an excess of formaldehyde, urea forms an amorphous precipitate, which is soluble in hot water with partial decomposition and is insoluble in alcohol, ether and cold water.<sup>1</sup> It appears to vary greatly in composition, according to the alkalinity of the solution in which it is produced.<sup>2</sup>

From formaldehyde and urea in neutral solution, Goldschmidt<sup>3</sup> obtained both dimethylolurea and a compound,



insoluble in water. From neutralized solutions of corresponding proportions of urea and formaldehyde, Dixon<sup>4</sup> obtained mono- and di-methylolurea, after allowing to stand for 1 to 2 days.

<sup>1</sup> Goldschmidt, *Chem.-Ztg.*, 21, 460 (1897); German Pat. 97,164; *Cf.* (1898), II, 523.

<sup>2</sup> Einhorn, *Hamburger, Ber.*, 41, 24 (1908).

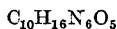
<sup>3</sup> *Cf.* (1897), II, 194, 737.

<sup>4</sup> *Trans. Chem. Soc.*, 113, 246 (1918).

On heating neutral aqueous solutions of urea and formaldehyde coagulated masses separate, resembling albumen in appearance, the formation and composition of which have been investigated by van Laer.<sup>1</sup> He found that if the components are present in the ratio of 1:1, interaction occurs between 5 molecules urea and 7 molecules formaldehyde. The formula of the product is



If the proportion of formaldehyde is doubled, so that the components are present in the ratio 1:2, then 3 molecules of urea interact with 7 molecules formaldehyde, and the composition of the product is

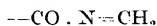


Finally, if an excess of formaldehyde is used, 3 molecules of urea interact with 11 molecules of formaldehyde, forming a substance  $\text{C}_{14}\text{H}_{10}\text{N}_6\text{O}_7$ . All the products must be considered to be polymers of the simplest empirical formulae given above. The two last-mentioned compounds slowly eliminate formaldehyde on boiling with water.

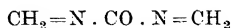
As is shown by the above facts, the reaction between urea and formaldehyde varies with the acid, alkaline or neutral solution in which it occurs. In all cases there is ample opportunity for the formation of mixtures and, therefore, for resin formation.

By careful operation in alkaline or neutral solution the reaction can be interrupted at such a stage that methylol- or dimethylol-urea are obtained as pure crystalline solids which show no tendency to polymerization, but which are capable of further condensation.

In acid solution or on heating, the linkage



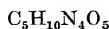
which is the medium of considerable polymerization, appears to be formed. Obviously, the reaction cannot proceed to the formation of the complex



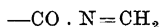
<sup>1</sup> *Bull. Soc. Chim. Belgique*, 28, 381 (1919); *C.* (1923), I, 902.



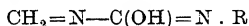
as is shown, for example, by Goldschmidt's reaction, with an excess of formaldehyde, in which the product has the composition



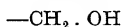
and in which 2 molecules of urea are condensed with 3 molecules of formaldehyde. This follows from the behaviour of dimethylolurea on heating and on prolonged treatment of its solution with dilute hydrochloric acid, by which means water and formaldehyde are liberated with formation of Goldschmidt's compound or of similar products. It may be concluded that the presence of at least one free hydrogen atom in the second amino group is necessary in order that the group,



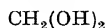
should be able to exercise its polymerizing tendency, that is, that the resinophoric or polymerizable group may perhaps have the following structure—



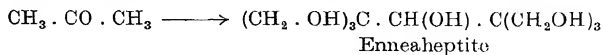
**Ketone-formaldehyde Condensation Products.** According to the investigations of B. Tollens and his pupils,<sup>1</sup> formaldehyde reacts with aliphatic aldehydes and ketones in presence of lime or baryta and water, in such a manner that the hydrogen atoms attached to the carbon atoms adjoining the carbonyl group are all ultimately replaced by the group



formaldehyde reacting as though it were methylene glycol,



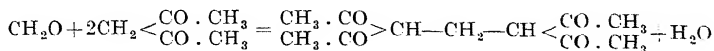
The carbonyl group is then reduced to a primary or secondary alcoholic group. It has only been found possible to isolate the polyalcohols so obtained from ketones in the form of their lactones or anhydrides. Thus, for example, the anhydride of enneheptite is obtained from acetones.<sup>2</sup>



<sup>1</sup> *Ann.*, 265, 316 (1891); 276, 82 (1893); 289, 36, 46 (1896); *Ber.*, 36, 1341 (1903).

<sup>2</sup> M. Apel, B. Tollens, *Ann.*, 289, 46 (1896).

The following reaction of a diketone, which occurs in presence of diethylamine or piperidine, and which leads to the formation of a tetrakone, is of interest.<sup>1</sup>



By using weak alkalis, such as magnesium hydroxide, borax, sodium phosphate, sodium or potassium carbonate, and so forth, or a small proportion of caustic alkali, *ketobutanol*,



was obtained from equimolecular proportions of formaldehyde and acetone; this is a liquid, boiling point 110° C., miscible with alcohol and ether, but which thickens and becomes insoluble on prolonged standing.<sup>2</sup>

By heating ketobutanol for a short period with caustic alkalis, C. Ellis<sup>3</sup> obtained an insoluble, infusible product, which is proposed as an amber substitute. The liquid ketone-alcohol may also be mixed with fillers, such as asbestos, mica, zinc oxide, sawdust, and so forth, and then heated in moulds to form moulded solids.

When equimolecular proportions of formaldehyde and acetone are condensed in the presence of a large proportion of alkali, a completely amorphous substance is obtained, of the empirical formula,



which was first discovered by Alphonse Werner,<sup>4</sup> and was recently further investigated by Arno Müller,<sup>5</sup> who determined its molecular weight in glacial acetic acid solution and so arrived at the formula,



<sup>1</sup> M. Scholtz, *Ber.*, 30, 2296 (1897); E. Knoevenagel, W. Buschhaupt, *Ber.*, 31, 1025 (1898).

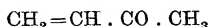
<sup>2</sup> C. (1910), II, 347, 1421; German Pat. 223,207, 227,177 (1910); U.S. Pat. 981,669, 991,734-5 (1911); see also U.S. Pats. 981,668, 989,993 (1911). These patents also deal with the homologues.

<sup>3</sup> U.S. Pat. 1,557,571 (1922); C. (1926), I, 1723; *Kunstst.*, 16, 116 (1926).

<sup>4</sup> *Proc. Chem. Soc.*, 20, 196 (1904); C. (1905), I, 221.

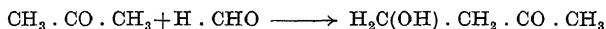
<sup>5</sup> *Ber.*, 54, 1142 (1921).

According to its composition, this substance might be supposed to be a polymerized methyleneacetone, but the intermediate product which should then be produced, monomeric methyleneacetone,

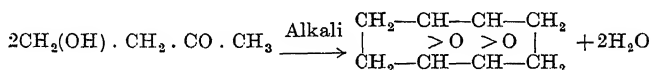


has never been isolated. From the behaviour of the amorphous substance to bromine and permanganate, Werner concludes that it cannot possibly be unsaturated. Müller confirmed this view, and also found that the oxygen atom had lost all its activity for reagents for ketones. It was also found to be easily nitratable.

On attacking the substance with permanganate in alkaline solution a mixture of fatty acids and of carbon dioxide was obtained, from which Müller concludes that ketobutanol is first formed—



which then liberates water and is transformed as follows—



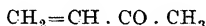
According to Müller, the resin is obtained by mixing 75 gm. of 40 per cent formaldehyde with 60 gm. acetone and pouring the mixture rapidly into a mixture of 50 c.c., 30 per cent caustic soda solution, and 200 c.c., 96 per cent alcohol. Any heat of reaction is suppressed by cooling. After standing for 36 hours the reddish-brown reaction product is poured into 2 litres of water. The reddish-brown substance which is precipitated is filtered on a Buchner funnel, washed with water and dried on a porous tile. The yield is 50 to 60 gm.

The crude product has a definite smell of hexenone, especially when moist, which can be removed by treating the dried product with alcohol. It is purified by recrystallization from ethyl or methyl alcohol, the product so obtained having a micro-crystalline structure. The purified product has a slightly yellow-orange colour and is tasteless and odourless when dry. It is

remarkable that on boiling with water, the smell of hexenone, to which reference has already been made, reappears.<sup>1</sup>

The product of the condensation is soluble in ethyl and methyl alcohols, acetone and benzene, less soluble in ether, almost insoluble in ligroin, water and dilute caustic alkali, but comparatively easily soluble in glacial acetic acid. On heating in a test-tube the product swells, carbonizes and gives a smell of burning, whilst small, dark brown drops of oil condense on the sides of the tube and are also carbonized if quickly heated. By the Beckmann freezing-point method in glacial acetic acid the purified product shows a molecular weight of 121.5. Theory for  $C_8H_{12}O_2 = 140$ .

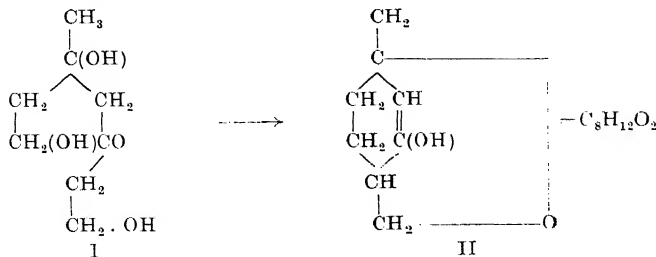
It is interesting to note that A. Wohl and A. Prill<sup>2</sup> succeeded in obtaining methyleneacetone,



by distilling ketobutanol with the addition of zinc chloride. When this product was distilled without zinc chloride a yellow viscous residue was obtained, which was probably a dimethylol-acetone, in which 2 hydroxyl groups could be identified by acetylation, although the ketonic group could not be identified.

The condensation products obtained under alkaline conditions have often been proposed as resin substitutes, or for the

<sup>1</sup> It is possible that an additive action occurs similar to that which must be assumed for the formation of diacetone-alcohol from acetone under the influence of alkali. The product so formed (I), would then be capable of transformation into a cyclic compound (II), which is no longer a ketone, and would yield a cyclohexenone derivative on hydrolysis.



<sup>2</sup> *Ann.*, 440, 139 (1924); *C.* (1925), I, 651; see also Bayer & Co., German Pat. 222,551.

preparation of plastic masses.<sup>1</sup> For the latter purpose they possess the useful characteristic, particularly if prepared from more than 1 molecule of formaldehyde per molecule of acetone, that they are convertible into an insoluble condition by heating.

Thus, from 1 molecule formaldehyde and 1 molecule acetone, in presence of alkaline condensing agents, soluble synthetic resin gels, or synthetic resin solutions, are obtained<sup>2</sup> by adding about 0.01 molecule sodium hydroxide at 15° C. and distilling off the excess of acetone after completion of the reaction, leaving the soluble gel in the residue. If a solvent is added to the mixture before the reaction, such as alcohol or methylethylketone, the reaction must be assisted by increasing the proportion of condensing agent, or by warming. In this case, also, a soluble resin-gel is obtained. Resin solutions are obtained directly if very minute quantities of condensing agent only are employed (0.003 molecules sodium hydroxide), and if these are added during a prolonged period, for example, 7 times in 7 days, to an equimolecular mixture of acetone and formaldehyde. The products are used more particularly for varnishes.

Plauson<sup>3</sup> obtains an artificial wood-like product by causing equimolecular quantities of acetone and formaldehyde to interact in presence of fillers, such as wood-meal, mineral powders, and so forth, by the use of alkaline condensing agents, such as alkalis, ammonia, alkali carbonates and sulphides; the reaction may be carried out under pressure. After freeing from alkali, acetone, and so forth, and drying, the product can be moulded at pressures of 150–200 atmospheres and temperatures of 120–200° C. to form solid bodies, which are unattacked by alkalis, acids, and almost all organic solvents, and which possess good insulating properties. Plauson adds that such substances as shellac, cellulose esters, oils, waxes, phenol-aldehyde resins, soluble in acetone, and so forth, may be added.

<sup>1</sup> See patent summary by Aladin, *Kunstst.*, 18, 14 (1928). On the use of the iodized products as disinfectant powders, see Hertkorn, U.S. Pat. 901,709 (1908); C. Ellis, *Synthetic Resins*, pp. 224 *et seq.*

<sup>2</sup> W. Traxl, Chem. Institute, Dr. K. Stockert and Dr. W. Traxl, Austrian Pats. 96,433 (1919); 98,669 (1920); *C.* (1925), I, 2472; *Kunstst.*, 15, 184 (1925).

<sup>3</sup> German Pat. 337,960 (1922); U.S. Pat. 1,397,144 (1921); *C.* (1922), II, 539; British Pat. 156,137 (1920); *C.* (1921), II, 673; French Pat. 529,783; *Kunstst.*, 12, 47 (1922).

Moreover, the formaldehyde may be replaced by hexamethylenetetramine, or by acetaldehyde, although the latter produces products which resinify with less facility.

A white, insoluble synthetic resin is obtained<sup>1</sup> if one molecule of a ketone is caused to interact with six molecules of formaldehyde, or the corresponding quantity of paraformaldehyde or hexamethylenetetramine, in the presence of alkalis or of other substances of alkaline reaction. From acetone and formaldehyde a white, tasteless and odourless powder is so obtained, of the formula



of infusible character, insoluble in organic solvents, which is unattacked by acids and alkalis and burns with extreme difficulty. Its insulating power is very high.

C. Ellis<sup>2</sup> first points out that the use as condensing agents of alkali carbonates or mixtures of disodium phosphate with a small amount of sodium hydroxide is preferable to that of strong alkalies, as the use of the latter leads to the production of dark red or brownish resinous masses, which are also very brittle. He obtains plastic masses from aliphatic ketones and formaldehyde, by first producing a soluble intermediate product which is then, with or without the addition of a catalyst and of further formaldehyde, converted into a mass which rapidly changes into the insoluble state on heating. The product obtained from 1 molecule acetone and about 2 molecules of aqueous formaldehyde, in presence of 25 per cent of sodium carbonate, calculated on the weight of the acetone, by gentle warming, initially to 50–60° C. and afterwards to 90–110° C., is soluble in alcohol and in a mixture of alcohol and benzene. The solution in methyl alcohol, to which the usual filling agents may be added, is carefully treated with alcoholic potassium hydroxide solution, with cooling, is then evaporated to dryness in a vacuum and hardened as rapidly as possible in suitable moulds under pressure at about 166° C. Insoluble and

<sup>1</sup> Plausons Forschungsinstitut G. m. b. H., German Pat. 351,349 (1920); *Kunstst.*, 12, 133 (1922); *C.* (1922), IV, 253.

<sup>2</sup> U.S. Pat. 1,514,508–9 (1922); *C.* (1925), I, 1138; see also C. Ellis, *Synthetic Resins*, p. 226; U.S. Pat. 1,482,929 (1921); *C.* (1925), I, 907; U.S. Pat. 1,502,945 (1922); *C.* (1925) I 908.

infusible horny masses are obtained, resembling tortoise-shell or bone. In order to produce light coloured, ivory-like products, a mixture of acetone, paraformaldehyde and aqueous sodium phosphate solution is gently warmed, the aqueous layer rejected, and the remainder dried in a vacuum at 70–80° C. The thick, water-clear syrup which is so obtained, is then carefully treated, with cooling, with concentrated aqueous potassium hydroxide solution, poured into moulds, allowed to stand in these for some time, and then heated to 120° C. for about an hour. White pigments, blanc fixe, magnesia, asbestos, and so forth, may be added to the soluble intermediate product as fillers and in order to modify the colour.

Synthetic resins, soluble in various solvents, are obtained<sup>1</sup> if the condensation between aldehydes and ketones is caused to take place in the presence of colophony, terpene hydrocarbons, or di-olefines, by means of alkalis, alkali sulphides or alkali carbonates, to which small amounts of salts containing much carbon dioxide may be added, and the products of condensation may be finally heated to 200–300° C. In order to obtain synthetic resins soluble in oil, small amounts of phenol esters, linseed oil, and similar oils are added; siccatives may be added in addition. The degree of solubility of the synthetic resins depends on the duration of the condensation process, on the temperature which is maintained and the character of the alkali which is used, and the same applies to the hardness. Those products which melt at high temperatures are completely soluble in chloroform and dichlorhydrin only, partially soluble in alcohol and acetone and insoluble in benzene. In the examples given, the ketones used comprise acetone and methylethyl-ketones, and the aldehydes, formaldehyde, furfural and paraldehyde.

As the above information shows, acetone is a substance which forms resins with the greatest facility with formaldehyde in alkaline solution. On the other hand, according to the investigations of C. Ellis,<sup>2</sup> methylethyl ketone appears to be

<sup>1</sup> Plauson's Forschungsinstitut G. m. b. H. German Pat. 389,241 (1920); C. (1924), I, 1716; *Kunstst.*, 14, 71 (1924).

<sup>2</sup> *Synthetic Resins*, p. 227.

less suitable. Cyclohexanones and fatty aromatic ketones have, however, been recommended as suitable for the production of synthetic resins.

Cyclohexanone reacts with equimolecular proportions of formaldehyde in the presence of acids (sulphuric acid) or alkalies (caustic soda) on heating, to form a resin, which is washed, dried and heated to 130–135° C. until a sample becomes hard and transparent on cooling.<sup>1</sup> The product is easily soluble in alcohol, ether, acetone, chloroform, amyl acetate, benzene, toluene and cyclohexanone. The resin forms colourless varnishes which give very lustrous, very clear and completely odourless coats which are satisfactorily fast to light. According to C. Ellis, especially colourless resins are obtained if mild alkalies and anhydrous formaldehyde are used. The resin from cyclohexanone becomes insoluble on continued heating. In place of hexanone, methycyclohexanone may be used for the condensation.<sup>2</sup> As both materials are products of the reduction of phenol, the production of resins by these methods appears to be a practicable proceeding.

*Fatty-aromatic ketones*, such as acetophenone, ethylphenylketone, methylnaphthylketone, and so forth, when treated with formaldehyde, or with compounds yielding that substance, in the presence of alkaline condensing agents, form resin-like substances which are resilient, hard and of pale colour, do not melt, and which dissolve in aromatic hydrocarbons and their halogen derivatives, tetrahydronaphthalene, carbon tetrachloride, trichlorethylene, acetone, ethyl acetate, cyclohexanol and linseed oil. The coatings obtained with such solutions are satisfactorily fast to light.<sup>3</sup>

**Condensation Products from Hydrocarbons with Formaldehyde.** The principal hydrocarbons to be considered for the production of resins from hydrocarbons and formaldehyde are aromatic hydrocarbons, indene or terpene hydrocarbons.<sup>4</sup>

<sup>1</sup> Badische Anilin- und Soda-Fabrik, German Pat. 339,107 (1918); *C.* (1921), IV, 714; French Pat. 514,929.

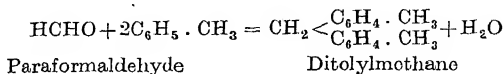
<sup>2</sup> On condensation products from cyclohexanol and formaldehyde in presence of alkali hydroxides, see U.S. Pat. 1,557,521; *C.* (1926), I, 1723.

<sup>3</sup> Aktien-Ges. für Anilin-Fabrikation, German Pat. 402,996 (1921); *C.* (1925), I, 308; *Kunstst.*, 15, 84 (1925).

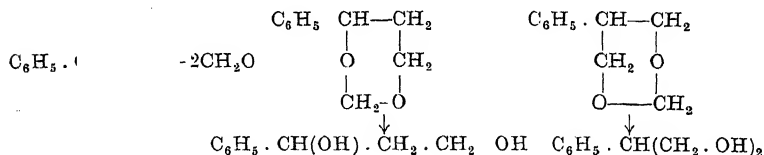
<sup>4</sup> See patent summary by Aladin, *Kunstst.*, 17, 282 (1927).



Aliphatic aldehydes, or preferably their substitution products, such as chloral, their polymerized derivatives or acetals, condense very smoothly, even at the ordinary temperature, with aromatic hydrocarbons and their substitution products, the solvent employed being usually glacial acetic acid, and the condensing agent, concentrated or fuming sulphuric acid.<sup>1</sup> The reaction proceeds as follows—<sup>2</sup>



Formaldehyde combines with a whole series of *unsaturated terpene hydrocarbons*, in 20 to 30 per cent of sulphuric acid, or in glacial acetic acid containing 10 per cent of sulphuric acid. The products obtained are either primary alcohols, or more frequently, glycol-methylene ethers or glycol acetates, which form glycol on saponification.<sup>3</sup> Thus, styrol forms phenyl-propyl glycols, as follows<sup>4</sup>—



The two types of reaction illustrated above probably represent the main outlines of these condensations. It may be anticipated that in presence of an excess of formaldehyde this takes part in various further reactions with the primary condensates, by which means all the conditions for the production of resinous products are fulfilled. In the reaction of indene with formaldehyde it must be assumed that the attack takes

<sup>1</sup> J. Houben, *Die Methoden der organischen Chemie*, II, 861 (1925); on colour reactions of formaldehyde with naphthalene, fluorene, etc., in presence of concentrated sulphuric acid, see H. Ditz, *Chem. Ztg.*, 31, 445, 486 (1907); who also refers to the earlier literature.

<sup>2</sup> A. Baeyer, *Ber.*, 5, 1098 (1872); 6, 223 (1873); 7, 1190 (1874); O. Zeidler, *Ber.*, 7, 1180 (1874); O. Fischer, *Ber.*, 7, 1191 (1874); O. Fischer, *J. prakt. Chem.* (2), 79, 557 (1909).

<sup>3</sup> J. Houben, *loc. cit.*, II, 1010.

<sup>4</sup> See B. Prins, *C.* (1918), I, 163; (1919), III, 1001; (1920), I, 423.

place at the methylene group,<sup>1</sup> thus affording the possibility for the development of a highly polymerized system.

The most important group of these resins is that comprising the condensation products from naphthalene and formaldehyde, which are generally soluble in hydrocarbons, chlorinated hydrocarbons and carbon disulphide, and more or less slightly soluble in alcohol, acetone, and so forth. The course of the reaction and character of the products are dependent on the nature of the components, the character and concentration of the condensing agent and the temperature and duration of the reaction.<sup>2</sup>

Information regarding the production of these resins on a technical scale is supplied by the investigations of P. Folchi, who recommends the following procedure—

100 grm. finely-ground naphthalene are mixed with 80 c.c., 30 per cent formaldehyde solution, and 100 c.c. sulphuric acid of 66° Be, are then added in small portions with continuous stirring or shaking. The mass is then warmed on the water-bath under reflux at 80° C. for 1½ to 2 hours, with occasional stirring. A semi-solid, granular or solid mass is thus obtained, which is washed twice with hot water, then with ammonia or caustic soda solution in order to remove traces of acid, and, finally, again with hot water. The product is dried at about 80° C. for 4 to 5 hours. In order to produce varnishes it is melted with a little turpentine, which causes the separation of an aqueous acid layer (which must be removed); the remainder, which may consist of a granular mass, is stirred with purified solvent naphtha and warmed. The highest possible yield, about 100 to 110 per cent of the naphthalene, is only attainable with the above concentration of sulphuric acid, with pure naphthalene and with the above quantities. A higher reaction temperature than 80–90° C. would cause risk of partial carbonization and lead to harder products. It is especially important to wash free from acid, as the mass does not dry in presence of acid. A batch was prepared as follows

<sup>1</sup> Compare the reaction with benzaldehyde, which leads to a benzylidene indene; J. Thiele, A. Bühner, *Ann.*, 347, 265 (1908); W. Wislicenus, W. Hentrick, *Ann.*, 436, 11 (1924).

<sup>2</sup> M. Folchi, *Chem. Ztg.*, 46, 714 (1922).

with acid of 60° Be.: 100 grm. naphthalene, 80 grm. 40 per cent formaldehyde solution, and 120 grm. sulphuric acid were heated for 3 hours to 90–95° C. In this way a yield of only 80 to 90 per cent of the naphthalene was obtained.

Already in 1907, the Badische Anilin- und Soda-Fabrik<sup>1</sup> described the production of such resinous products, by the interaction of more than  $\frac{1}{2}$  molecule formaldehyde with 1 molecule naphthalene in presence of sulphuric acid. The resins proved suitable for the production of varnishes, sealing-wax, waterproof fabrics,<sup>2</sup> and so forth. They are soluble in benzene, toluene, xylene, naphtha and chlorobenzene, and insoluble in water, alcohol, turpentine oil and linseed oil. For example, 100 parts of powdered naphthalene were added with stirring to a mixture of 80 parts 30 per cent formaldehyde solution with 100 to 115 parts sulphuric acid of 66° Be, and the temperature raised to 100° C. and maintained at that level, by cooling if necessary. The thick mass obtained after 1½ hours was treated with hot water, allowed to set and washed with water to remove the acid. It is purified, for example, by dissolving in benzene and precipitating any unchanged naphthalene with a small quantity of alcohol. The product is a yellow-brown vitreous mass.

Examples are also given in which larger proportions of formaldehyde and sulphuric acid are used. Similar products are produced by Bayard de la Vingtrie,<sup>3</sup> which are intended to replace rubber for the production of ebonite.

A further process is described by Bayer & Co.,<sup>4</sup> and is thereby characterized that the concentration of the sulphuric acid in the reaction mixture is not over 60 per cent. The products which are produced are soluble in acetone, benzene, solvent

<sup>1</sup> The reaction between naphthalene and methylal, in the presence of concentrated sulphuric acid, which results in the formation of dinaphthylmethane, was investigated by J. Grabowsky in 1874 (*Ber.*, 7, 1605).

German Pat. 207,743; *C.* (1909), I, 1208; U.S. Pat. 898,307 (1908); *Kunstst.*, 2, 95 (1912); British Pat. 16,245 (1907); French Pat. 336,664 (1908); Swiss Pat. 44,096; *Kunstst.*, 1, 313 (1911); 2, 93 (1912).

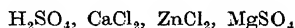
<sup>2</sup> German Pat. 303,891 (1917); *C.* (1919), IV, 329.

<sup>3</sup> French Pat. 493,569 and patent of addition 22,278; *Kunstst.*, 12, 172 (1922); *C.* (1921), IV, 471.

<sup>4</sup> German Pat. 349,741 (1918); *C.* (1922), IV, 50.

naphtha, carbon tetrachloride and carbon disulphide, and are completely colourless resins. Unchanged naphthalene is removed by steam distillation. The naphthalene may be replaced by phenanthrene, anthracene, benzene or xylene.

More recent processes are concerned with the reduction of the quantity of contact agent. Thus, condensation is effected by heating under pressure, in presence of extremely small quantities of dehydrating contact agents, with or without stirring; or mixtures of more than one contact agent, or of such contact agents with weak contact agents or with inert materials are employed.<sup>1</sup> Suitable contact agents are, for example,



and suitable hydrocarbons are benzene, naphthalene, phenanthrene, anthracene and their homologues and reduction products, whilst suitable aldehydes are those of both the aliphatic and the aromatic series. According to another process,<sup>2</sup> aromatic hydrocarbons and their derivatives, with the exception of those containing acid or basic groups, are heated without the application of pressure with aldehydes or substances which liberate aldehydes, in the presence of such limited quantities of phosphoric acid or of halogen hydride, and conveniently in the presence of solvents such as glacial acetic acid, that products soluble in linseed oil are obtained. The products, which are soluble in hydrocarbons, linseed oil, varnish oil and turpentine oil, are intended for use in the production of varnishes.

Resin-like materials of similar properties have also been obtained from formaldehyde or aldehydes in general, and the halogen or other addition products of anthracene and phenanthrene,<sup>3</sup> from formaldehyde and halogenated naphthalene<sup>4</sup>

<sup>1</sup> Chemische Fabriken, Dr. Kurt Albert G. m. b. H., German Pat. 387,836 (1918); *C.* (1924), II, 549; *Kunstst.*, 14, 139 (1924).

<sup>2</sup> Farbwerke vorm. Meister, Lucius & Brünig, German Pat. 403,264 (1919); *C.* (1925), I, 307; *Kunstst.*, 15, 84 (1925).

<sup>3</sup> German Pat. 420,443 (1922) of Bakelite Gesellschaft m. b. H.; *C.* (1926), I, 2253.

<sup>4</sup> German Pat. 332,334 (1918) of Akt.-Ges. f. Anilin-Fabrikation; *C.* (1921), II, 652; *Kunstst.*, 11, 94 (1921).

(which are soluble in fatty oils and in turpentine oil), and from formaldehyde and the hydrogenation products of naphthalene, the products being soluble in linseed oil and turpentine oil.<sup>1</sup>

Resin-like condensation products have also been obtained from formaldehyde with terpene hydrocarbons and with indene.

G. Orloff<sup>2</sup> obtained a brownish-red resin, which was partially soluble in alcohol, benzene, toluene, glacial acetic acid and ether, from 100 parts turpentine oil, 200 parts sulphuric acid of 66° Be, and 55 to 66 parts of 40 per cent formaldehyde solution, by maintaining certain conditions of reaction. After decanting the molten mass and heating this to 290° C., a brownish-black hard resin was obtained, soluble in benzene, toluene, glacial acetic acid and ethyl acetate, but only partially soluble in alcohol and petroleum ether.

The formation of resins from spruce oil and paraformaldehyde under the influence of concentrated hydrochloric acid was investigated by C. Ellis.<sup>3</sup>

To produce the indene-formaldehyde condensation product,<sup>4</sup> 100 parts of indene and 100 parts of 30 per cent formaldehyde solution are mixed with 5 to 10 parts concentrated hydrochloric acid and boiled for 5 hours under reflux until the indene has disappeared and a thick, clear oil has separated at the bottom of the liquid. This is drawn off, washed with sodium carbonate solution and dried. It is viscous in the cold, limpid when warm, and dries in the air to a solid film which may be employed as a linseed oil substitute.

When considering the various condensations with formaldehyde described in this section, it must be remembered that such substances as crude naphthalene,<sup>5</sup> turpentine oil,<sup>6</sup> and indene are condensed or polymerized with formation of resinoid

<sup>1</sup> Akt.-Ges. f. Anilin-Fabrikation, German Pat. 305,575 (1917); *C.* (1921), II, 607; *Kunstst.*, II, 29 (1921); Tetralin (f. m. b. H., German Pat. 333,060 (1918); *Kunstst.*, II, 94 (1921).

<sup>2</sup> German Pat. 191,011 (1906); *Angew.*, 21, 229 (1908).

<sup>3</sup> *Synthetic Resins*, 342.

<sup>4</sup> M. Claass, German Pat. 310,783 (1918); *Kunstst.*, 9, 329 (1919); *C.* (1920), II, 38.

<sup>5</sup> Weissgerber, Kruber, *Ber.*, 53, 1551 (1920).

<sup>6</sup> Reynaud, French Pat. 419,860; *Kunstst.*, I, 156 (1911); German Pats. 262,093, 267,476.

products, by concentrated sulphuric acid alone. These reactions will, therefore, accompany the actual formaldehyde condensation to a variable degree, depending on the conditions of reaction.

### Products from Formaldehyde with Various other Substances.

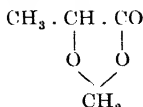
**LACTIC ACID.** Zimmermann<sup>1</sup> heats lactic acid for a long period in a vacuum, gradually raising the temperature from 100–200° C. On condensing the product with formaldehyde or paraaldehyde an odourless resin is obtained, the colour of which is from light yellow almost to black, according to the purity of the lactic acid employed; this resin is soluble in chloroform and glacial acetic acid, less soluble in benzene, and insoluble in ether and alcohol. On the methylenelactic acid obtained from formaldehyde and lactic acid, see page 204.

**AMMONIUM SULPHIDE.** According to H. Dieser,<sup>2</sup> resinous products are obtained by the action of formaldehyde on ammonium sulphide, which may be utilized either alone or in suitable solvents, such as tetrachlorethane, pentachlorethane, chloroform, and so forth. These resins are very stable to alkalies, and are recommended for the production of coatings for electric conducting wires, for lining vessels, for impregnating wood, fibres, and so forth.

**AMMONIUM SULPHOCYANIDE.** With formaldehyde this substance yields amorphous, yellow masses, which are not very stable and practically insoluble, and which possess a very unpleasant smell on warming.<sup>3</sup>

**AROMATIC SULPHAMIDES.** Colourless, odourless resins, which are fast to light and are soluble in acetone and benzene, are obtained by heating arylsulphamides and their N-substitution

<sup>1</sup> German Pat. 305,775 (1917); *C.* (1918), II, 84; *Kunstst.*, 8, 274 (1918); 9, 8 (1919). On the methylenelactic acid obtained from formaldehyde and lactic acid,



see L. Henry, *Ann.*, 292, 31, Note 3 (1896); C. A. Lobry de Bruyn, W. A. van Ekenstein, *Rec. trav. chim. Pays-Bas* 20, 340 (1901); 21, 316 (1902).

<sup>2</sup> German Pat. 246,038 (1910); *Kunstst.*, 3, 88 (1913).

<sup>3</sup> Schmerda, *Angew.*, 30, 176 (1917); C. Ellis, *Synthetic Resins*, S. 316.

products with formaldehyde, either alone or with condensing agents.<sup>1</sup>

**SULPHAMIDES OF TETRAHYDRONAPHTHALENE.** These substances and their N-monosubstituted derivatives condense with formaldehyde to form resins which are fast to light, which are insoluble in alcohol, acetone, cyclohexanol and amyl acetate, and which have a higher melting point than the products from aromatic sulphamides.<sup>2</sup>

### CONDENSATES WITH ALDEHYDES OTHER THAN FORMALDEHYDE, AND WITH KETONES<sup>3</sup>

The reactions of formaldehyde are omitted from those of aldehydes in general, here to be discussed, as although that substance shows the same general behaviour as other aldehydes, it is able to take part in many condensations peculiar to itself. For this and other reasons it has already been discussed in the preceding paragraph.

The most various substances may play the part of the other component in condensations with aldehydes, but compared with formaldehyde, other aldehydes show a greatly reduced reactivity. In most condensations, ketones act in an analogous manner to aldehydes, although there are differences regarding the resin-forming capabilities of the two classes of condensates.

**Phenol-aldehyde and Phenol-ketone Condensates.** According to the investigations of A. von Baeyer and his pupils, Jäger, E. ter Meer, Fabinyi, and Steiner,<sup>4</sup> both aliphatic and aromatic aldehydes and ketones condense with phenols and their ethers, for which reactions concentrated sulphuric acid, glacial acetic acid, alkali bisulphate,<sup>5</sup> fuming hydrochloric acid,

<sup>1</sup> Farbwerke vorm. Meister, Lucius & Brüning, German Pat. 359,676; *C.* (1923), II, 340; German Pat. 369,644; *C.* (1923), II, 922. On the use of the resin obtained by condensation of p-toluenesulphamide with formaldehyde as a constituent of cellulose esters, see H. A. Gardner, U.S. Pat. 1,564,664 (1925); *C.* (1926), I, 2266.

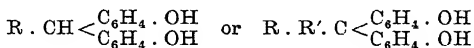
<sup>2</sup> Farbwerke vorm. Meister, Lucius & Brüning, German Pat. 376,473; *C.* (1923), IV, 600.

<sup>3</sup> The products obtained from acetylene in presence of mercury salts as catalysts under the influence of auxiliary catalysts, also belong to the class of aldehyde condensates; see Consortium für elektrochemische Industrie, French Pat. 593,338; Austrian Pat. 103,106; *C.* (1926), II, 1791.

<sup>4</sup> *Ber.*, 5, 25, 280, 1095 (1872); 7, 1197, 1201 (1874), 11, 283, 287 (1878).

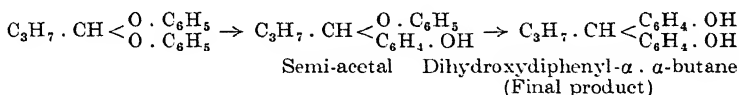
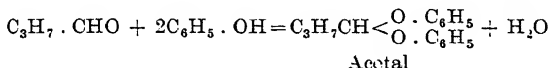
<sup>5</sup> Akt.-Ges. f. Anilin-Fabrikation, German Pat. 23,775; *Ber.*, 16, 2541 (1883).

hydrochloric acid gas, tin chloride, and other substances may be used as condensing agents. The ethers and esters of phenols react with much more difficulty than the free phenols,<sup>1</sup> a fact which is due to the character of the reaction. The final products are usually dihydroxydiphenylmethane derivatives of the following constitution—

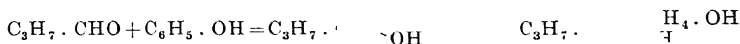


These products are of a homogeneous crystalline character.

Free phenols apparently always react by first forming compounds of an acetal character,<sup>2</sup> a reaction which naturally cannot occur with phenol ethers or esters, which accounts for the relative difficulty with which these condense. The acetals which are first formed are then transformed during the further course of the reaction, more particularly during prolonged heating, with migration of the aldehydic residue into the nucleus, thus forming isomeric compounds, the above-mentioned dihydroxydiphenylmethane derivatives,<sup>3</sup> a reaction which might obviously occur in stages. For example, the reaction between n-butyraldehyde and phenol may be supposed to pass through the following intermediate stages—



The following substances may also be obtained as reaction products, not in large amounts, excepting under special conditions, but probably always as accompanying impurities—



As long as the reaction has not proceeded to the formation of a uniform final product, this must always consist of a mixture

<sup>1</sup> L. Claisen, *Ann.*, 237, 264 (1887).

<sup>2</sup> See L. H. Baekeland, H. L. Bender, *J. Ind. Eng. Chem.*, 17, 225 (1925); *Kunstst.*, 15, 135, 176, 216 (1925); 16, 53, 114 (1926); Gomberg, *J. Am. Chem. Soc.*, 37, 2575 (1915); MacKenzie, *Chem. Soc. Trans.* 121, 1695 (1922).

<sup>3</sup> See L. Claisen, *Ber.*, 19, 3317 (1886).

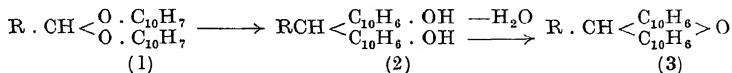


of substances similar in character, as the various reactions naturally occur simultaneously. From the definition of the resinoid state, all the requirements for the production of such a state are present. In actual fact, the intermediate products are resinous materials, whilst the final product, or the pure acetal,<sup>1</sup> is always a crystalline substance.

According to Baekeland and Bender, the butyraldehyde-phenol crystalline final product shows the same molecular weight, in benzene, as the resinous intermediate product, which was considered to be the semi-acetal, but which is presumably actually a mixture of acetal, semi-acetal, and final product. The acetal-like character of the intermediate product is shown by the fact that it forms a mono-sodium salt only with sodium hydroxide, whereas the crystalline dihydroxydiphenyl- $\alpha$ ,  $\alpha$ -butane forms a di-sodium salt. By heating the resin for 1 hour to 260° C., the crystalline end-product can be obtained with a yield of 80 per cent.<sup>2</sup>

In the technical production of resins, the development of resinoid characters is further assisted by the fact that small quantities of non-reacting raw materials increase the complexity of the mixture, and also that mixtures of isomeric cresols and so forth may be used. It is to be noted that according to Dianin,<sup>3</sup> methylenediphenols are dissociated by acids.

The tendency of polyvalent and polynuclear phenols<sup>4</sup> to form anhydride end-products in the reaction with aldehydes or ketones is of interest. Thus,  $\beta$ -naphthol and aldehyde<sup>5</sup> form the acetal (1), then the diphenol (2), and, finally, the anhydride (3), insoluble in alkali—



<sup>1</sup> See *Kunstst.*, 15, 176 (1925); L. Claisen, *Ber.*, 19, 3317 (1886), describes, for example, benzalglycol-di- $\beta$ -naphthylacetal as a crystalline substance of m.p. 203–205° C.

<sup>2</sup> A similar effect was observed in the author's experiments on the corresponding propane derivative.

<sup>3</sup> See *Ber.*, 25 R, 334 (1892).

<sup>4</sup> See C. Liebermann, S. Lindenbaum, *Ber.*, 37, 1171 (1904).

<sup>5</sup> L. Claisen, *Ann.*, 237, 264, 271 (1887); *Ber.* 19, 3316 (1886); A. Claus, E. Trainer, *Ber.*, 19, 3010 (1886).

On the other hand,  $\alpha$ -naphthol forms the normal diphenol, soluble in alkali. According to Claisen, one may expect all phenols in which the para-position is already occupied, that is in which the aldehyde residue has therefore to assume the ortho-position, to form such inner anhydrides by the reaction with aldehydes. This standpoint should certainly be considered in any explanation of the conversion of the formaldehyde-phenol resins into products insoluble in alkali. (See pages 154 *et seq.*)

The reaction between phenols and ketones proceeds in an exactly analogous manner. It proceeds more rapidly with increasing amount of the hydrochloric acid used as a condensing agent, which must not exceed a certain limit,<sup>1</sup> and the smaller the molecular weight of the ketone. The addition of ferric chloride has been found to promote the reaction.<sup>2</sup> The preparation of a melting-point diagram showed the presence of an intermediate product, consisting of a molecular combination of 1 molecule acetone with 2 molecules phenol.<sup>3</sup>

The fact is of interest that  $\alpha\beta$ -unsaturated ketones or their halogen-hydride addition products (for example, those of benzalacetone) react with phenols in the presence of acid condensing agents, with ring formation<sup>4</sup>:



The technical development of the processes described in this section will be dealt with later in a special section.

**Aldehyde and Ketone Condensates.** Both aldehydes and ketones can easily be converted into condensation products, in which the carbonyl group of one molecule reacts with a methylene or methyl group adjoining the carbonyl group of a second molecule, with elimination of water. The reaction is

<sup>1</sup> A. Dianin, *Ber.*, 25 R. 334 (1892).

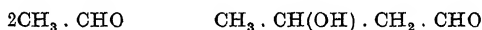
<sup>2</sup> Arno Meyer, *Chem.-Ztg.*, 45, 632 (1921).

<sup>3</sup> Jul. Schmidlin, R. Lang, *Ber.*, 43, 2898 (1910).

<sup>4</sup> Weiler-ter-Meer, German Pat. 357,755; C. (1922), IV, 890.

further characterized by the fact that the initial condensation products so formed are able to interact in the same manner, in which way four or more molecules may ultimately be united. A further characteristic of the reaction is that it often leads to ring formation, especially in the case of ketone condensations, although it is also frequent with aldehyde condensations. Certain differences of behaviour exist between aldehydes and ketones, for which reason it appears desirable to deal with them separately.

**Aldehyde Condensations.** Aldehydes are characterized by the fact that on autocondensation they first form stable additive compounds, which may then be transformed into true condensation products with elimination of water. In the case of aromatic aldehydes these additive compounds are the *benzoin*s, whilst the aliphatic aldehydes, which are more important for resin production, similarly form the *aldols*. Thus, acetaldehyde undergoes the following reaction :

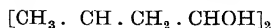


forming  $\beta$ -hydroxy-butyraldehyde, aldol, or acetaldol; the condensing agent used in this case may be zinc chloride in presence of water, aqueous solutions of salts with an alkaline reaction, dry potash, soda, dilute hydrochloric acid, and many others.<sup>1</sup>

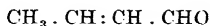
On standing, acetaldol becomes viscous with evolution of heat, forming paralldol, a water-soluble dimeride, which crystallizes with difficulty.<sup>2</sup> This capacity for polymerization is common to all aldols ( $\beta$ -hydroxyaldehydes) and also to the  $\alpha$ -hydroxyaldehydes, and may be considered as a factor favourable to resin formation. On distillation in vacuo the products revert to the monomolecular condition.

<sup>1</sup> See *Beilstein*, I, 824.

<sup>2</sup> Wurtz, *Compt. rend.* 76, 1166 (1873); 83, 255, 1259 (1876); L. Kohn, *Monatsh.* 21, 80 (1880); Nowak, *Monatsh.* 22, 1140 (1881); the tendency of aldol to polymerize is attributed to the tendency to association of an oxygen bridge:



Water elimination from aldol occurs on warming to 84–85° C.,<sup>1</sup> and also, for example, by the action of glacial acetic acid,<sup>2</sup> forming crotonaldehyde,



On heating acetaldol to 125° C.,<sup>3</sup> tetraldan is formed,



a crystalline substance of melting point 112–113° C. which is easily soluble in benzene, chloroform, ether and alcohol, but soluble with difficulty in acetone and ligroin. This substance shows no reactions for either an aldehyde or an aldol, and no reactions indicating a double linkage. A dialdan,



has been obtained from a mixture of aldehyde, water, and hydrochloric acid on prolonged standing.<sup>4</sup> When pure it forms a crystalline substance of melting point 139–140° C., which differs from paralldol by being but slightly soluble in cold water, but freely soluble in hot water and very easily soluble in boiling alcohol.

As will be seen from the above examples, which could be multiplied indefinitely, condensation can occur in many ways, even when acetaldol is alone involved as an intermediate product. It can be foreseen that under suitable conditions condensation may occur with the formation of still larger molecules than that of tetraldan, and that these substances may eliminate water by intramolecular reactions. Thus the production of more highly condensed products of resinous character is explained by the justifiable assumption of the production, in this manner, of mixtures of substances similar in

<sup>1</sup> Grignard, Reif, *Bull. Soc. Chim.* (4), 1, 116 (1907).

<sup>2</sup> Wurtz, *Compt. rend.*, 74, 1363 (1872).

<sup>3</sup> Wurtz, see Lobry de Bruyn, *Bull. Soc. Chim.* (2), 42, 164 (1884); *Bijl. Rec. trav. chim. des Pays-Bas*, 19, 173 (1900); see *Beilst.*, I, 826.

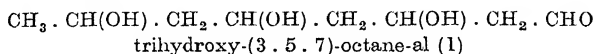
<sup>4</sup> Wurtz, *Compt. rend.*, 83, 1259 (1876); 92, 1373 (1881); *Bull. Soc. Chim.* (2), 28, 169 (1877); see *Beilst.*, I, 325.

character. Recent investigations (*vide infra*) have shown that a resinous product of the approximate composition,



is formed, the molecular weight of which can be determined.

The reaction of acetaldehyde in presence of condensing agents does not, however, lead exclusively to the formation of acetaldol, but aldols of higher molecular weight are also formed, among which



has been isolated. The separation of the various condensation products is very difficult. Higher aldols of this character may, obviously, form compounds of very varied character by the elimination of water.

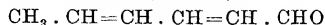
Cannizaro's reaction and oxidation processes may also exert a certain influence on resin formation during the condensation of aldehydes in the presence of alkaline reagents.<sup>1</sup>

Any intermediate formation of crotonaldehyde, a liquid fairly easily soluble in water, having an odour which is at first fruity, but which becomes penetrating later, is not especially favourable to resin formation, as this is only induced by the action of such reagents as sodium amalgam and hydrochloric acid.<sup>2</sup> Yet crotonaldehyde forms aldols, for example, with acetaldehyde,<sup>3</sup> which may be assumed to be more susceptible to resinification. In fact, crotonaldehyde has been recommended, together with acetaldehyde and aldol, as the most suitable primary material for various technical processes.

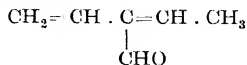
<sup>1</sup> See Hammarsten, *Ann.*, 421, 293 (1920).

<sup>2</sup> Lieben, Zeisel, *Monatsh.*, 1, 823 (1880); see *Beilst.*, I, 729.

<sup>3</sup> On the formation of hexadienal, probably



and of  $\alpha$ -vinyl-crotonaldehyde,

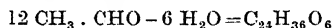


by the condensation of metalddehyde in presence of sodium acetate, see S. Zeisel and M. Neuwirth, *Ann.*, 433, 121 (1923); *C.* (1924), I, 158.

The resinous product obtained on condensing acetaldehyde with alkalis, the so-called aldehyde resin, was first discovered by Döbereiner,<sup>1</sup> and further investigated by Liebig,<sup>2</sup> Weidenbusch,<sup>3</sup> Ciamician,<sup>4</sup> Puchot,<sup>5</sup> Ekekrantz,<sup>6</sup> and Hammarsten.<sup>7</sup> Ekekrantz succeeded in separating the resin into two isomers,  $\alpha$ - and  $\beta$ -aldehyde resins, by precipitation from acetone and ether. The resins were found to contain 2 ethylene linkages, as they added 4 atoms of chlorine or bromine. On oxidation a white acid,



was obtained. Otherwise, no well-defined derivatives could be isolated. According to Ekekrantz, the composition of the resin corresponded approximately to the following formula,



Whereas previous workers had used fairly concentrated aqueous or alcoholic solutions, Hammarsten carried out the resin formation in dilute aqueous solutions, using N/5 to 8N solutions of the aldehyde and N/5 to 2N-KOH solutions, by which means he obtained two resins.

For example, 10 litres of 2N acetaldehyde solution, prepared from 440 gm. pure, freshly distilled acetaldehyde and water, were cooled below 10° C., and 10 litres of 10 per cent aqueous KOH solution were then gradually added with stirring. The liquid was cooled at first, so that the temperature did not exceed 15° C. After yellow coloration and turbidity had been produced, the mixture was allowed to stand for 5 to 6 days at room temperature, with frequent shaking.

The liquid was then neutralized with about 4½ litres of 2N-hydrochloric acid, so that a filtered sample was exactly neutral to phenol-phthalein some minutes after the addition of the acid. The deeply orange-coloured resin was filtered and

<sup>1</sup> Schweigg, *Journ.*, 38, 327.

<sup>2</sup> *Ann.*, 14, 140 (1835).

<sup>3</sup> *Ann.*, 5, 25 (1833); 14, 133, (1835); 66, 153 (1848).

<sup>4</sup> *Monatsh.*, 1, 199 (1880).

<sup>5</sup> *Ann. Chim.* (6), 9, 423 (1886); *Ber.*, 20, III, 64 (1887).

<sup>6</sup> *Arkiv. f. kemi.*, 4, 15 (1912); *C.* (1912), II, 1194.

<sup>7</sup> *Ann.*, 421, 293 (1920); *C.* (1921), I, 209

washed with cold water until the chloride reaction disappeared. The filtrate was treated with 600 c.c. of concentrated hydrochloric acid, which caused the separation of a pale yellow precipitate, which was also filtered and carefully washed. Both resins were dried at the ordinary room temperature at 10 mm. pressure, first over sulphuric acid, and then over phosphorus pentoxide.

Both resins were extremely finely subdivided, very easy to filter and to wash. The yield amounted to 265 grm. red resin and 55 grm. yellow resin, or about 46 per cent of the aldehyde used.

The red resin is a deeply orange-red powder, practically insoluble in water and in alkalis. The colour becomes lighter on keeping. It is readily soluble in alcohol, glacial acetic acid, chloroform and acetone, commences to sinter at 96° C., but only melts completely at 120° C., and is then immediately decomposed.

The yellow resin is of a very pale straw colour, slightly soluble in water with a clear yellow colour, and fairly easily soluble in alkalis with a dark yellow colour; it is also soluble in alcohol, glacial acetic acid, chloroform and acetone. It commences to sinter at 105° C., and melts at 120°-130° C. It commences to decompose at over 200° C. Elementary analyses and molecular weight determinations of these resins and of those obtained by Ekekrantz gave the following results—

	Elementary Analysis		Molecular Weight (in Acetone and Glacial Acetic Acid)
	% C	% H	
Ekekrantz—			
$\alpha$ -resin . . . .	68.32	8.30	438
$\beta$ -resin . . . .	68.60	8.44	429
Hammarsten—			
Red resin . . . .	69.19	7.82	427
Yellow resin . . . .	66.73	7.68	404
Calculated for $C_{24}H_{26}O_6$ . . .	68.58	8.58	420

Thus the aldehyde resin which is produced consists of at least two constituents of different composition, namely, the ordinary aldehyde resin, which is initially red and which was investigated by Ekekrantz and separated into  $\alpha$ - and  $\beta$ -resin, and the yellow resin, which is soluble in alkali. Hammarsten further states that the formation of aldehyde resin should not be considered as an end-reaction in the condensation of acet-aldehyde, but that on the contrary the various substances: acetal, ethyl alcohol, higher aldols, yellow and red resins are simultaneously produced in an acetaldehyde solution.

On distillation with zinc dust aldehyde resin yields benzene homologues, and on oxidation or in a potash melt it yields aromatic carboxylic acids.<sup>1</sup> The well-known example of the formation of cymol from citral<sup>2</sup> shows how easily ring formation occurs in such condensations, often with displacement of double linkages. It should be mentioned that polyvinyl alcohol also appears to be present in aldehyde resin, although attempts to convert acetaldehyde into its isomer, vinyl alcohol, have not yet met with success.<sup>3</sup> On the technical development of these aldehyde condensations for the manufacture of synthetic resins, see the section on "Aldehyde Resins."

**Ketone Condensations.** The formation of additive compounds, the aldols, which is characteristic of aldehydes, is shared by ketones to a very limited extent only,<sup>4</sup> thus eliminating a very important resin-forming factor in the condensation of ketones. On the other hand, the possible variations in the manner of condensation of ketones are much more numerous than with aldehydes on account of the presence of two methyl or methylene groups adjoining the carbonyl group, which leads to the condensation of acetone, for example, to the most various products, including mesityl oxide, phoron, mesitylene, isophoron and the xylitones. Cyclohexanone, in particular, has been much used for resin-forming ketone condensations.<sup>5</sup>

<sup>1</sup> See *Beilstein*, I, 598, and also the authors cited above.

<sup>2</sup> See Houben, *Methoden*, II, 879 (1925).

<sup>3</sup> H. Staudinger, K. Frey and W. Starck, *Ber.*, 60, 1786 (1927).

<sup>4</sup> A. Franke, Th. Köhler, *Ann.*, 433, 314 (1923).

<sup>5</sup> On condensation to dodecahydrotriphenylene and other compounds, see C. Mannich, *Ber.*, 40, 153, 159 (1907); see also O. Wallach, *Ber.*, 40, 70 (1907); Karl Kunze, *Ber.*, 59, 2085 (1926); *C.* (1926), II, 2573.



Cyclic ketones, such as cyclohexanone and cyclohexylidene hexanone, are converted into resinous condensation products by heating with alkaline condensing agents.<sup>1</sup> For example, 200 parts of cyclohexanone are heated with 100 parts alcoholic caustic potash (2 parts methyl alcohol to 1 part potassium hydroxide) for 20 hours under pressure at 200–220° C. The resins are soluble in alcohol, benzene, cyclohexanone and linseed oil.

By the condensation of cyclohexanone with mineral acids (50 per cent sulphuric acid), or such substances as zinc chloride, resins are obtained which are soluble with difficulty in alcohol, but soluble in benzene and in linseed oil.<sup>2</sup>

Resins from cyclohexanone, and from cyclic ketones in general, may be utilized together with other resinous products or with cellulose derivatives.<sup>3</sup>

**Condensates from Aldehydes with Ketones.** Compared with formaldehyde (see page 164), the other aldehydes play an unimportant part only as components for resin-forming condensations with ketones.

H. Dreyfus<sup>4</sup> obtained resinous condensation products from acetaldehyde and cyclohexanone or their homologues, by heating the components in the presence of acid or basic condensing agents, with or without the addition of diluents or solvents, such as alcohol or benzene. For example, 100 parts of cyclohexanone, 100 parts of alcohol, and 1 part of 50 per cent sodium hydroxide solution are gradually mixed at 90° C. with 250 parts of 25 per cent acetaldehyde solution and boiled for 3 to 4 hours. After distilling off the alcohol an oil remains, which gradually changes to a solid resin. When condensed so energetically with higher aldehydes that the initially-formed products, of low molecular weight, are further condensed,

<sup>1</sup> Badische Anilin- und Soda-Fabrik, German Pat. 337,993 (1919); *C.* (1921), IV, 426, 912; *Kunstst.*, 12, 37 (1922); British Pat. 146,498; *Kunstst.*, 12, 23 (1922).

<sup>2</sup> Badische Anilin- und Soda-Fabrik, British Pat. 170,351 (1920); *C.* (1922), II, 330; *Kunstst.*, 10, 39 (1920); Swiss Pat. 89,060; *Kunstst.*, 12, 14 (1922); see also Ruhemann, *J. Chem. Soc. Trans.*, 95, 109 (1909).

<sup>3</sup> Badische Anilin- und Soda-Fabrik, German Pat. 420,414 (1924); *C.* (1926), I, 1300; *Kunstst.*, 16, 76 (1926). See also patent summary by Aladin, *Kunstst.*, 18, 14 (1928).

<sup>4</sup> British Pat. 181,575 (1921); *C.* (1923), IV, 730; *Kunstst.*, 13, 125 (1923).

cyclohexanone and its derivatives yield resins of good solubility, which can be used in the varnish and varnish oil industries.<sup>1</sup> The use of alkaline or acid condensing agents is advantageous, as is also operation under pressure.

Meunier<sup>2</sup> produces resins from furfural, or furfural and ketones. The reaction takes place by heating furfural, either alone or admixed with ketones, or with aldehydes such as acetaldehyde, in the presence of an inorganic or organic base, and, if desired, under increased pressure.<sup>3</sup>

Thus by slowly adding 1 part of a mixture of equal volumes of acetone and furfural to 3.5 parts of 30 per cent caustic alkali solution, boiling under reflux, and then heating for a short time, a resin was obtained which, when washed and dried, had a yellow colour, and dissolved in acetone, benzene, or a mixture of 23 volumes of furfural and 77 volumes of alcohol, forming varnishes. It is stated that by heating with linseed oil, the resin can be obtained in a form suitable for the production of oil varnishes.

Similar products were obtained by G. H. Mains and M. Phillips<sup>4</sup> by using concentrated caustic alkali solutions. For example, a dark-brown resin, suitable for the production of wood varnishes, is obtained from furfural and methylethylketone in presence of 50 per cent caustic soda solution at 25° C. By combining this with fatty oils, black stoving enamels are obtained.

L. T. Richardson<sup>5</sup> obtains a condensation product from acetone and furfural in another manner. The components are mixed and then gradually added to caustic soda solution, maintaining the temperature at 60–70° C. by cooling. Phosphoric acid is then added until the reaction is slightly acid, and the resulting product washed with water and dehydrated at 100–105° C. It then forms a viscous liquid, holding a mass of

<sup>1</sup> Badische Anilin- und Soda-Fabrik, British Pat. 403,646 (1922); *C.* (1925), I, 309; see German Pat. 339,107; *C.* (1921), IV, 714.

<sup>2</sup> French Pat. 472,384 (1913); *Kunstst.*, 12, 23 (1923).

<sup>3</sup> On the course of the reaction, see, for example, Itizo Kasiwagi, *C.* (1926), II, 892.

<sup>4</sup> *Chem. Met. Eng.*, 24, 661 (1921); *C.* (1922), II, 445; *Kunstst.*, 11, 189 (1921); 13, 89 (1923); U.S. Pat. 1,441,598 (1921); *C.* (1925), I, 2471.

<sup>5</sup> U.S. Pat. 1,584,144 (1925); *C.* (1926), II, 1206.

crystals in suspension; this is mixed with acid condensing agents, by preference naphthalenesulphonic acid, together with washed asbestos, sawdust, cellulose, and so forth. On heating to 180° C. in moulds under pressure, hard, tough, insoluble black masses are formed.

Further, Plauson<sup>1</sup> obtains plastic masses, or soluble, fusible resins, which are further transformed on heating, quite generally from ketones (such as acetone, methylethylketone, diethylketone, vinylalkylketones, pinacolines, mesityl oxide, phoron, acetone oil and acetophenone) and furfurol, or substances which liberate furfurol (such as furanecarboxylic acid and furoin), by interaction in presence of condensing agents, such as alkaline lyes or acids.

We must finally refer to experiments by H. A. Gardner and A. Knauss,<sup>2</sup> on the production of resins from acetone with furfurol, aldol, and paraldehyde. The products are intended for use as additions to cellulose-ester varnishes. They are prepared in the presence of acid or basic condensing agents, to which colophony or cellulose esters may be added.

**Condensates from Aldehydes with Amines or Ammonia.** These products also are of but little importance as artificial resins compared with the corresponding formaldehyde products. (See page 156.)<sup>3</sup>

**ACETALDEHYDE.** With naphthylamine acetaldehyde forms a resinous condensation product at the ordinary temperature in the presence of a solvent, such as benzene, which is either resilient or of soft character, and is soluble in acetone, alcohol, benzene, and so forth.<sup>4</sup>

**ACETALDEHYDE, ALDOL, CROTONALDEHYDE.** Varnishes ready for application are obtained<sup>5</sup> by condensing aniline, toluidine, xyldine, or  $\alpha$ -naphthylamine (or mixtures of these) in

<sup>1</sup> Plauson's Forschungsinstitut G. m. b. H., German Pat. 386,013 (1920); *C.* (1924), I, 1716; *Kunstst.*, 14, 71 (1924).

<sup>2</sup> *Ind. Eng. Chem.*, 20, 1928 (1928).

<sup>3</sup> On use for the production of oily mixtures for soaking insulating tape, see U.S. Pat. 1,594,982 (1926); *C.* (1926), II, 2857.

<sup>4</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 300,685 (1917); *C.* (1922), II, 879.

<sup>5</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 372,855; *C.* (1923), IV, 600; I. G. Farbenind., A.-G., British Pat. 270,433; French Pat. 612,758; *C.* (1927), II, 934; German Pat. 451,734; *C.* (1928), I, 122.

varnish solvents, such as benzene or tetraline, with acetaldehyde, aldol, or crotonaldehyde, or mixtures of these, with acid (such as oxalic acid), as a condensing agent, by heating to 80–100° C. The condensation product from acetaldehyde and aniline in acid solution (see page 66) has been proposed as an "antioxygen" for rubber.<sup>1</sup>

Hubert Rauch<sup>2</sup> obtains resinous condensation products by heating benzylidene compounds of aromatic amines to high temperatures in the presence or absence of neutral, basic, or acid accelerators, to which solvents or diluents may be added. A resin of analogous properties is obtained by heating  $\alpha$ -naphthylamine with benzaldehyde, solvent naphtha and 25 per cent hydrochloric acid under reflux. After the removal of the aqueous layer the solution can be used as a varnish. The resins themselves are insoluble in acids and alkalies, slightly soluble in alcohol, but very soluble in benzene and linseed oil.

FURFUROL. Meunier<sup>3</sup> obtained a resin, soluble in alcohol and benzene, by heating furfural with aniline, the 15 to 20 per cent solution of which, when used as a varnish, formed brilliant black coats, which are converted into an insoluble coating of black enamel by heating to 50–60° C. The actual condensation could be accelerated by dehydrating agents, such as zinc chloride.

G. H. Mains and M. Phillips<sup>4</sup> investigated the behaviour of a whole series of amines with furfural. Aniline, m-nitraniline, p-toluidine and  $\alpha$ -naphthylamine react on heating to 150–200° C., with formation of black resins, whilst  $\beta$ -naphthylamine and m-toluylenediamine react at 25° C. In the case of o-toluidine, 1-methyl-2-amino-4-isopropyl-benzene and crude xylydine, it is necessary to add strong hydrochloric acid (specific gravity 1.19), whilst amylamine, dimethylaniline and m-phenylenediamine show no resin formation with furfural, even on heating for 3 hours to 200° C. Furfural forms no crystalline compounds with p-nitraniline, benzidine, or toluidine at room temperature. The resinous products, which soften and liquify at

<sup>1</sup> Naugatuck Chemical Co., U.S. Pat. 1,626,784; C. (1927), II, 752.

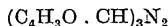
<sup>2</sup> German Pat. 401,726 (1922); C. (1925), I, 308.

<sup>3</sup> French Pat. 472,384.

<sup>4</sup> Chem. Met. Eng., 24, 661 (1921); U.S. pat. 1,441,598.

30° to 100° C., are insoluble in water, slightly soluble in turpentine oil, soluble in benzene, acetone and alcohol, and very soluble in furfural. The solutions are recommended for varnishing wood. The products may be converted into oil varnishes.

By the action of high temperatures on furfuramide,



which is obtained from furfural and aqueous ammonia, both Meunier, and also Mains and Phillips, obtained a resin soluble in benzene, which is an impure furfuralin.<sup>1</sup>

**Condensates from Aldehydes and Hydrocarbons.** BENZALDEHYDE. On condensing benzaldehyde with benzene homologues ( $\text{C}_8$  and over), in presence of concentrated sulphuric acid, resins are obtained which resemble colophony.<sup>2</sup> These are insoluble in water, acids, and alkalis, slightly soluble in alcohol and methyl alcohol, and easily soluble in acetone, ether, chloroform, ethyl acetate and aromatic hydrocarbons.

ACROLEIN. Moureau and Dufraissee<sup>3</sup> obtain resinous condensation products, capable of being hardened, from acrolein and organic compounds, such as hydrocarbons, their derivatives, alcohols, ethers, and so forth, in the presence of basic catalysts. (See also page 171 *et seq.*)

## CONDENSATES WITH ALCOHOLS

Whereas simple alcohols of low molecular weight, such as methyl alcohol, form simple ethers or esters with phenols and acids respectively, the relations become more complicated with products of higher molecular weight, such as benzyl alcohol, and particularly with poly-alcohols and allied compounds, such as the carbohydrates. On the one hand other reactions occur, such as nuclear condensations, and on the other the homogeneity of the processes diminishes rapidly, so that in place of well-defined products, mixtures are formed which may show the properties of resins. Some of these resins are convertible into insoluble and infusible products, which, of course, increases

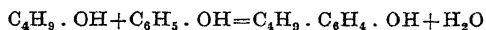
<sup>1</sup> See Dubosc, *Kunstst.*, II, 59 (1921); Trickey, Miner, Brownlee, *J. Ind. Eng. Chem.* (1923), 65.

<sup>2</sup> Farbw. vorm. Meister, Lucius & Brünig, German Pat. 365,541; *C.* (1923), II, 922.

<sup>3</sup> French Pat 528,498; *C.* (1922), IV, 894.

their value considerably. For this reason this class of resin-forming processes is of exceptional interest.

**Condensates from Alcohols and Phenols.** Even the higher aliphatic alcohols<sup>1</sup> show with phenols, in presence of dehydrating agents, such as zinc chloride, sulphuric acid, glacial acetic acid, alkali bisulphate, magnesium chloride, and so forth, not only the power of normal ether formation, but also the property of interaction with the nucleus, that is, of substitution of the aromatic nucleus by the alcohol radicle. Thus, for example, isobutyl alcohol forms p-isobutylphenol with ordinary phenol.<sup>2</sup>



Benzyl alcohol reacts with phenol in a similar manner, forming p-hydroxydiphenylmethane.

The same reaction is presumably an intermediate stage in resin formation from poly-alcohols, in which more or less stable ethers must be assumed to be primary or accompanying products, as may be concluded, for example, from the formation of glycerine mono-phenol ethers on heating glycerine with phenol in presence of sodium acetate.<sup>3</sup> As, moreover, poly-alcohols are alone used for practical resin manufacture, and these substances are able to eliminate water with formation of unsaturated compounds, and formation of oxygen bridges, which promote aggregation,<sup>4</sup> there are numerous possibilities for the formation, not merely of resin, but of resins capable of further transformation, that is, of hardening.

*Glycerine.* J. McIntosh and E. Yeakle<sup>5</sup> recommend heating

<sup>1</sup> On the reaction of cellulose with benzene, see Nastjukow, *C.* (1902), II, 576

<sup>2</sup> See J. Houben, R. Kempf, *Methoden d. org. Chem.*, Third Edition (1925), Vol. II, 854; A. Liebmam, *Ber.*, 15, 150 (1882); see also L. von Dobrzycki, *J. prakt. Chem.* (2), 36, 390 (1887).

<sup>3</sup> Zivkovic, *Monatsh.*, 29, 951 (1908); Elotzky, *Monatsh.*, 30, 663 (1909).

<sup>4</sup> See also B. Rajendra Nath Sen, Nripendra Nath Sarkar, *J. Amer. Chem. Soc.*, 47, 1079; *C.* (1925), II, 187; H. K. Drew and W. N. Haworth, *J. Chem. Soc., London* (1927), 775; *C.* (1927), II, 43.

<sup>5</sup> Canadian Pat. 229,395 (1922); *C.* (1924), I, 1717; *Ind. Eng. Chem.*, 19, 111 (1927); see also *Farbe und Lack* (1927), 285, 287 (ref.); *Kunstst.*, 14, 71 (1924). On the replacement of glycerine by epichlorhydrin, allyl-alcohol, glyceraldehyde, dihydroxyacetone, and so forth, with the use of various catalysts, such as  $H_2SO_4$ , bromine, pyridine, and sulphur chloride, and the addition of hardening agents, such as formaldehyde, hexamethylenetetramine, benzidine-acetone or acetone-sodium disulphite, see Diamond State Fibre Company, U.S. Pats. 1,642,078 and 1,642,079; *C.* (1927), II, 2476-77.

a mixture of 700 parts glycerine, of specific gravity 1.25, and 1,000 parts phenol, in presence of 10 parts sulphuric acid of specific gravity 1.84 to 160–190° C. The water formed by the reaction is allowed to distil, and the process is considered to be finished when 350 parts of water have been condensed. The resultant liquid is then cooled and neutralized with lime, chalk, or barium carbonate. The dark resin so obtained is an initial condensation product, that is, it can be melted or dissolved, and is converted by sufficiently prolonged and intensive heating into an insoluble, infusible product. It is advisable to accelerate the hardening process by adding 4 to 12 per cent of formaldehyde. The product, which is known as "Acrolite," has recently been proposed as a substitute for "Resole" resins, which are phenol-formaldehyde condensation products.

*Carbohydrates.* G. Mauthner<sup>1</sup> prepared resinous condensation products from cellulose and phenols, using mineral acids as condensing agents, which were fusible or infusible according to the conditions of reaction. With increasing amounts of the condensing agent, consisting of sulphuric or hydrochloric acid, the velocity of the reaction is increased, and may even be almost instantaneous, and leads at once to the final product. The required temperature depends on the quantity of acid and on the nature of the desired product. The reaction, which starts in the cold and proceeds more rapidly on heating, first leads to the production of liquid products, which are further converted into plastic masses, which can be kneaded, and finally to solid, resinous substances. Fusible or infusible products are thus obtained, according to the temperature employed and the duration of the reaction.

Similar resins were obtained from cellulose or carbohydrates and phenol by Hartmuth,<sup>2</sup> Claessen,<sup>3</sup> McIntosh,<sup>4</sup> E. Novotny, and J. Romieux,<sup>5</sup> and were also found to be hardened by

<sup>1</sup> German Pat. 247,181; *Kunstst.*, 3, 88 (1913).

<sup>2</sup> German Pats. 326,705, 328,783 (1919); *C.* (1921), II, 143, 235.

<sup>3</sup> British Pat. 160,482 (1919); *C.* (1921), IV, 269.

<sup>4</sup> Canadian Pat. 229,152; *C.* (1923), IV, 730.

<sup>5</sup> Canadian Pat. 249,166 (1922); British Pat. 208,193 (1922); *C.* (1926), II, 1,473; *Kunstst.*, 16, 225 (1926).

formaldehyde, hexamethylenetetramine or furfuramid. Stearic acid and other substances are recommended as plasticizers.<sup>1</sup>

Resinous products have been obtained with phenols and starch<sup>2</sup> and hexoses.<sup>3</sup>

The reaction of hexoses with phloroglucin was investigated by C. Counciler,<sup>4</sup> who found that condensation occurred between a molecule of each substance with elimination of 3 molecules of water. In some cases, however, the products were found to be formed by the combination of 3 molecules of each substance, with elimination of 8 molecules of water. Ethers are probably formed. C. Ellis appears to suppose that furfural is first formed under the influence of the catalyst, as may be concluded from the fact that he includes the resins obtained from cellulose with phenols among the furfural resins.<sup>5</sup> It is impossible to disagree with the view that this may occur, at least in part. The accompanying formation of phenol-furfural resins would at least explain the otherwise strange fact that the reaction is not promoted by alkali,<sup>6</sup> and also that the resinous products are intensively dark coloured.

**Condensates from Poly-alcohols and Polyvalent Acids.** In the esterification of polyvalent acids with poly-alcohols complicated reactions may naturally be expected, leading to the production of mixtures. This is the case, for example, in the syrupy products obtained by van Bemmelen as primary products on heating equivalent quantities of succinic acid and glycerine, or of citric acid with an excess of glycerine.<sup>7</sup> The

<sup>1</sup> V. Meigs, British Pat. 274,146.

<sup>2</sup> Diamond State Fibre Company, Canadian Pat. 229,396; *C.* (1924), I, 1717; British Pat. 221,553 (1923); French Pat. 567,315 (1923); *C.* (1926), II, 1474; *Kunstst.*, 16, 254 (1926).

<sup>3</sup> J. V. Meigs, U.S. Pat. 1,593,342 (1925); *C.* (1926), II, 1594. See also F. Konther, German Pat. 402,541 (1923); *C.* (1924), II, 2431; *Kunstst.*, 15, 12 (1925); see also German Pat. 380,764; *C.* (1923), IV, 731; Enamel by the joint use of molasses or sugar and phenols.

<sup>4</sup> *Ber.*, 28, 24 (1895).

<sup>5</sup> *Synthetic Resins and Their Plastics*, p. 220.

<sup>6</sup> Unpublished experiments by Scheiber and Noack.

<sup>7</sup> *Jahresber. Fortschr. d. Chem.* (1856), 603; (1858), 434; Funaro and Danesi, *do. do.* (1880), 799; Otto, see *Beilstein*, II, 612; Lourenço, *Ann. Chim.* (3), 67, 313 (1863); Oechsner de Coninck und Raynaud, *Compt. rend.*, 135, 1352 (1902).



"initial condensation product" obtained by L. Weisberg,<sup>1</sup> of fusible character and soluble in acetone, on treating phthallic acid with glycerine, should also probably be considered as a mixture of esters. The easy saponification of these products supports this view.

The reaction becomes more complicated on more prolonged and intensive heating, as other processes accompany esterification, such as ether formation, anhydride formation, the formation of unsaturated groups, and so forth. The results of such reactions are apparent in the form of reduction of the solubility in acetone and infusibility. Thus on heating the syrupy initial ester mixtures obtained by him to 200° C. for several hours, van Bemmelen obtained solid infusible substances. Weisberg, also, by further heating his soluble and fusible initial condensation product, was able to convert it into an intermediate product which was no longer soluble in acetone and no longer fusible, and which could only be moulded under the joint influence of heat and pressure. The reactivity with water, which still characterizes this product, which is, of course, disadvantageous in practice, can be completely removed by further prolonged heating, so that the ultimate product is fast to both cold and hot water.<sup>2</sup> It is remarkable that even this product is still soluble in glycerine.

The loss of solubility and fusibility shows that in the course of the condensation compounds are formed which possess the capacity for far-reaching association or polymerization. Regarding the actual reactions, which will, undoubtedly, vary greatly with the very great possible variations of the components, nothing is known. The increase in molecular weight which is possible by simple esterification, leading, for example, to the formation of a compound,

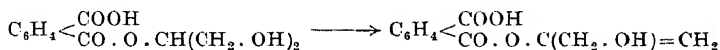


from equivalent quantities of phthallic acid and glycerine, does not appear adequate to explain the observed facts. From

<sup>1</sup> U.S. Pat. 1,413,144-5 (1922); *C.* (1923), IV, 368, 668; British Pat. 173, 225; *C.* (1922), II, 748.

<sup>2</sup> See also Watson Smith, according to C. Ellis, *Synthetic Resins and Their Plastics*, p. 292; Callahan, U.S. Pat. 1,108,329-30 (1914).

the fact that resin formation is considerably accelerated by replacing glycerine by polyglycerines,<sup>1</sup> it must be concluded that other chemical processes also occur, the most important of which is probably the formation of cyclic ethers. Such processes would explain why the increase in molecular weight ultimately leads to the formation of colloidal complexes. It is, however, possible that vinyl-derivatives are also formed to some extent, as might occur, for example, by the elimination of water from the  $\beta$ -mono-esters.



The di-esters might also form similar compounds.

A further possible explanation of the polymerizations which occur would be by the production of oxygen-containing rings, which might be produced by the opening out of polymeric complexes, as explained by H. Staudinger.<sup>2</sup>

The scope of the reaction is very considerable, as any polyvalent aliphatic or aromatic acids may be used with any polyalcohol. Even polyvalent inorganic acids are suitable. Thus, for example, a "resinoid" substance, which is, however, soluble in water, is obtained from boric acid and glycerine, and may be described as an "organic-inorganic synthetic resin."<sup>3</sup> This substance may also be considered as a link with the purely inorganic "resins," namely, the glasses. It is also of interest that the salts of phthallic acid and of nitrophthallic acid mono-esters with zinc, lead, copper, iron, and so forth, possess the characteristics of resins.<sup>4</sup>

Generally speaking, in the phthallic acid-glycerine products and the corresponding resins, the pure condensation reactions appear to be of far greater importance than in most other varieties of resin production.

Regarding the production of these products,<sup>5</sup> we have already

<sup>1</sup> L. Weisberg, R. S. Potter, U.S. Pat. 1,424,137 (1922); *C.* (1923), IV, 668; *Kunstst.*, 13, 125 (1923).

<sup>2</sup> *Helv. Chim. Acta*, 8, 306 (1925); *C.* (1925), II, 158.

<sup>3</sup> E. Fonrobert und F. Pallauf, *Chem. Umschau*, 33, 43 (1926).

<sup>4</sup> Commercial Solvents Corp., U.S. Pat. 1,618,209; British Pat. 250,265; French Pat. 612,976; *C.* (1928), I, 1337, 1584.

<sup>5</sup> See also the Patent Summary by Aladin, *Kunstst.*, 18, 68 (1928).

referred to very early investigations, particularly to those of van Bemmelen. But the condensation products of succinic and citric acids and of other aliphatic acids with glycerine are of very slight technical importance compared with the phthallic acid-glycerine resins, the so-called "Glyptals."<sup>1</sup> The first investigation of any such product was first carried out by Watson Smith in 1901.<sup>2</sup>

Smith heated a mixture of 2 molecules glycerine and 3 molecules phthallic anhydride for a long period almost to the boiling point. On cooling, a solid resinlike, completely-transparent product was obtained, which was insoluble in water, but soluble in an excess of glycerine on warming. The resin was easily saponified by caustic alkali solution. Its melting point was about 190° C.; at 220° C. it commenced to decompose and carbonize, although the mass was not yet completely melted. Smith recommended the product as a cement for glass and porcelain.

Callahan<sup>3</sup> found that in order to avoid permanent softness and stickiness of the resins the organic acid must be used in excess. For the production of the phthallic acid-glycerine product, for example, he gives the following instructions<sup>4</sup>—

One part by weight of glycerine and 2 parts by weight of phthallic anhydride are slowly heated. At 100° C. the mixture forms a clear liquid, and on further heating a small amount of distillation occurs. At 185° C. any further temperature rise should be avoided until distillation ceases. The product is then heated further, up to about 210° C., until the first stage of the reaction is completed. The completion of this stage is recognized by cooling small samples, which should then yield a hard, brittle, non-adhesive resin, which is yellowish and transparent.

On continuing the heating beyond 210° C. a further reaction occurs, with evolution of heat. At 275° C. the liquid commences to froth freely, and a brittle infusible mass is obtained, interspersed with bubbles.

<sup>1</sup> The name Glyptal for these resins has been protected by the Bakelite G. m. b. H., Berlin-Charlottenburg.

<sup>2</sup> *J. Soc. Chem. Ind.*, 20, 1075 (1901); C. Ellis, *Synthetic Resins*, p. 292.

<sup>3</sup> U.S. Pat. 1,091,732 (1914).

<sup>4</sup> U.S. Pat. 1,108,329 (1914); *Kunstst.*, 5, 165 (1915).

This formation of bubbles occurs even if the temperature of 210° C. is maintained. A dense, homogeneous mass can, however, be obtained if the transformation (polymerization) is carried out by heating for a prolonged period (e.g. 15 to 20 hours) at 85–100° C. or even at 135° C. The insoluble product softens at temperatures above 40° C., but only melts on decomposition. Alkali decomposes the resin, with formation of glycerine and phthallic acid.

The product so obtained is still sensitive to water, on lying in which it becomes white and cheesy, and is also not weather-proof. By further heating<sup>1</sup> to 180–250° C. for 5 to 10 hours, the condensation is completed and any remaining free glycerine is removed. The resin is then insoluble in all ordinary solvents, but is still soluble in glycerine as is the intermediate condensation product. It is not attacked by alkaline solutions in the cold. At 140° C. the resin becomes leathery and can be moulded.

Callahan also recommends the use of glycol and carbohydrates instead of glycerine; he also gives examples of the use of succinic, citric, malic<sup>2</sup> and camphoric acids.<sup>3</sup>

The production of mixed esters proved to have a favourable effect on the physical properties, more especially by reducing the brittleness. Thus, Arsem<sup>4</sup> obtained such a substance by first causing glycerine to interact with a quantity of an acid insufficient to saturate all the hydroxyl groups, and then continuing the esterification with another acid. The product can then be hardened as described above. Callahan<sup>5</sup> uses mixtures of acids, for example, 4 molecules phthallic anhydride and 6 molecules succinic acid, for condensation with 10 molecules glycerine. This product can also be hardened in the usual manner.

Arsem first showed that phthallic acid could be replaced by tartaric, glutaric, camphoric or malic acid, and the glycerine

<sup>1</sup> Callahan, U.S. Pat. 1,108,330 (1914).

<sup>2</sup> U.S. Pat. 1,091,627 (1914).

<sup>3</sup> U.S. Pat. 1,091,628 (1914); British Pat. 24,059 (1912) *Kunstst.*, 4, 76 (1914).

<sup>4</sup> U.S. Pat. 1,098,776–7 (1914).

<sup>5</sup> U.S. Pat. 1,108,332 (1914).

by glycol or mannite. For the further esterification the most various mono- and di-basic acids can be used, such as propionic, stearic, palmitic, oleic,<sup>1</sup> benzoic, lactic, salicylic, glycollic, chloracetic, chlorobenzoic or chloropropionic acids, which naturally influence the solubility, fusibility, hardening properties and character of the resultant resins.<sup>2</sup> Butyric acid,<sup>3</sup> shellac,<sup>4</sup> colophony and copal<sup>5</sup> have also been combined with phthallic acid.

Apart from combination with a second acid, endeavours have also been made to change the properties of the products by admixture with other materials.

In order to improve the elastic properties, Dawson<sup>6</sup> proposed the admixture of m-dinitrobenzene, ethyl benzoate, acetanilide and  $\beta$ -naphthol. According to Howell<sup>7</sup> and Dawson,<sup>8</sup> castor oil produces an improvement in the toughness and resilience of the resins. As the castor oil is undoubtedly changed by the formation of other esters at the high temperatures which are employed, its application should really be classified with the formation of mixed esters. This view is supported by the fact that considerable proportions of castor oil are used.

A further improvement in the production of resins from polyvalent alcohols is said to be achieved<sup>9</sup> by using the alcohols in a precondensed form. Thus on heating glycerine for half an hour to 280° C. in presence of  $\frac{1}{2}$  per cent sodium hydroxide or sodium acetate, condensation products are formed with considerable elimination of water, the so-called polyglycerines.

<sup>1</sup> On heating the resin from oleic acid, phthallic acid, and glycerine with sulphur, a rubber-like mass is formed; Arsem, U.S. Pat. 1,082,106 (1913); *Kunstst.*, 4, 157 (1914); British Pat. 9985 (1913); *Kunstst.*, 4, 117 (1914).

<sup>2</sup> If phthallic anhydride and glycerine are condensed in presence of sulphuric acid, subsequent addition of unsaturated fatty acids results in the formation of dark but very elastic products, which can be hardened; see British Thomson-Houston Co., British Pat. 252,394; French Pat. 616,463; *C.* (1928), I, 1336; Barret Co., U.S. Pat. 1,667,197-200; *C.* (1928), II, 293.

<sup>3</sup> Freidburg, U.S. Pat. 1,119,592 (1914); *Kunstst.*, 5, 215 (1915).

<sup>4</sup> L. Weisberg, U.S. Pat. 1,413,145 (1922); *C.* (1923), IV, 368.

<sup>5</sup> C. Ellis, U.S. Pat. 1,541,336 (1923); *C.* (1926), I, 797.

<sup>6</sup> U.S. Pat. 1,085,112 (1914).

<sup>7</sup> U.S. Pat. 1,098,728 (1914).

<sup>8</sup> U.S. Pat. 1,141,944 (1915).

<sup>9</sup> L. Weisberg, R. S. Potter, U.S. Pat. 1,424,137 (1922); *C.* (1923), IV, 668; *Kunstst.*, 13, 125 (1923).

These interact with phthallic acid, for example, much more rapidly than glycerine itself. (See above.)

The technical application of all these resins has so far been very small, owing to the high price of phthallic acid. According to C. Ellis, a small amount of phthallic acid-oleic acid-glycerine resin is used for coating electrodes which come into contact with litharge, owing to its resistance to litharge and water. The resin is applied in the form of a solution in acetone and is stoved after drying.

The soluble initial products are used for the production of varnishes, the solvent employed being mainly acetone, although cyclohexanone, diacetone-alcohol and mixtures of cyclohexanone with alcohol and of butyl alcohol with benzene have been stated to be useful. Better solubility in fatty oils, is attained, for example, by preparing the resins in the presence of suitable fatty acids.<sup>1</sup> After application, the coatings, which are readily attacked by water, must be hardened by heating for a considerable period. The danger of thickening of the varnish on admixture with basic pigments can be counteracted by pre-treatment of the resin with alkaline substances, such as lime, soda, baryta, and so forth.<sup>2</sup>

According to C. Ellis,<sup>3</sup> the products may be used with advantage as auxiliary components of modern cellulose nitrate varnishes such as are increasingly used, more especially for motor-cars. Although they cannot be directly incorporated with fatty oils, this can be achieved, according to L. V. Adams,<sup>4</sup> by dispersing the resinous product, jointly with the fatty oil to be used, such as linseed oil, tung oil, or castor oil, in any desired proportion, in a high boiling solvent, by heating. The following are recommended as suitable dispersing agents: benzyl benzoate, benzyl acetate, nitrobenzene, aromatic amines, phenols, benzyl alcohol, glycol diacetate, and so forth. After colloidal solution has been attained the solvent is distilled off, leaving a product which dissolves in the usual varnish

<sup>1</sup> British Thomson-Houston Co., British Pat. 284,349; E. J. du Pont de Nemours & Co., U.S. Pat. 1,667,189; C. (1928), II, 293.

<sup>2</sup> British Thomson-Houston Co., British Pat. 284,348.

<sup>3</sup> U.S. Pat. 1,529,056 (1924); C. (1925), II, 357.

<sup>4</sup> British Pat. 235,595 (1925); C. (1926), II, 1477; *Kunstst.*, 16, 254 (1926).

thinners, such as benzene, turpentine oil, and so forth. The films of the oil varnishes so produced are stated to be very elastic and durable, insoluble, infusible, and fast to oil and to heat.

The suitability of these resins for the production of moulded articles is due to the possibility of hardening, by careful heating, without the production of gas bubbles.<sup>1</sup> In this connection various proposals have been made for the method of mixing the resin with fillers. Thus, Callahan<sup>2</sup> adds 13 to 18 per cent of naphthalene, anthracene, and so forth, in order to facilitate the impregnation of the fillers. Further, the insoluble, already hardened, products are caused to swell by treatment with suitable solvents. In this condition, not only can they be moulded,<sup>3</sup> but they can be mixed with fillers, pigments, and shellac. In the latter case, after mixing, they are dried, ground, and finally moulded whilst hot.<sup>4</sup> In order to facilitate mixing with fillers, compounded resins are also used, to which phenol-formaldehyde resins,<sup>5</sup> copals or colophony<sup>6</sup> have been added. When additions of the latter kind are made, esterification of the free resin acids naturally occurs if, as recommended, the resin is present during the condensation process, or the mass is subsequently hardened. J. G. E. Wright<sup>7</sup> found that the soluble initial condensation products, to the solutions of which fillers may be added, are converted into hard, infusible products by heating for a short period (1 to 2 minutes) to high temperatures (about 240° C.) in the presence of finely-divided metallic oxides or metals, such as iron, thus accelerating the hardening process considerably. In order to convert the initial condensation product into a substance but very slightly soluble in

<sup>1</sup> Thus, for example, the product is heated for several weeks to 125° C.; see Bakelite Corp., U.S. Pat. 1,663,183.

<sup>2</sup> U.S. Pat. 1,108,331 (1914).

<sup>3</sup> British Pat. 23,776 (1912); *Kunstst.*, 4, 76 (1914); The British Thomson-Houston Co.; with Toluene, Benzine, Acetone, Chloroform, etc.

<sup>4</sup> L. Weisberg, U.S. Pat. 1,443,936 (1921); *C.* (1926), II, 1468; *Kunstst.*, 16, 253 (1926).

<sup>5</sup> L. Weisberg, U.S. Pat. 1,443,935 (1921); *Kunstst.*, 13, 90 (1923); British Thomson-Houston Co., British Pat. 250,949; Metropolitan-Vickers Electrical Co., British Pat. 253,519; *C.* (1928), II, 293.

<sup>6</sup> C. Ellis, U.S. Pat. 1,541,336 (1923); *C.* (1926), I, 797.

<sup>7</sup> British Pat. 236,591 (1925); U.S. Pat. 1,581,902; *C.* (1926), II, 1473; *Kunstst.*, 16, 254 (1926).

acetone, J. G. E. Wright and W. J. Bartlett<sup>1</sup> recommend heating it to high temperatures in a solvent of fairly high boiling point, such as diethyl phthallate. The product so obtained has no longer a corrosive action on metals, such as copper, and after mixing with fillers, if required, may be converted into the completely insoluble final product by heating for a short time to 180° C. It is used for the production of electrically insulating coatings and objects.

It is found that these resins have been found to be especially suitable for the production of Micanite objects, that is, articles produced from consolidated powdered mica. In this case hardening can be effected at higher temperatures than can be employed with other binding agents, such as phenol-formaldehyde resins, shellac, and so forth. Consequently, the finished objects so produced are correspondingly heat resistant, which, for example, enables commutator cones to be produced which will even withstand molten tin for a definite time.<sup>2</sup>

The identification of glycerine-phthallic acid resins offers no difficulty, as they are still sufficiently saponifiable, even after hardening, for the products of saponification to be easily identified in most cases.<sup>3</sup>

**Other Alcoholic Condensations.** De Laire<sup>4</sup> condensed 8 parts of phenol alcohols with 2 parts phthallic acid or phthallic anhydride, by boiling the components in alcoholic solution, then distilling off the alcohol and heating the residue to over 100° C. The resinous product so obtained was found to be soluble in alcohol, but became insoluble and infusible on further heating.<sup>5</sup>

According to a recent process of L. T. Sutherland,<sup>6</sup> phenol-alcohols are combined with cyclic ethers of the polyatomic

<sup>1</sup> British Pat. 235,589 (1925); French Pat. 604,198 (1925); *C.* (1926), II, 1475; *Kunstst.*, 16, 254 (1926); U.S. Pat. 1,634,969; A.E.G., German Pat. 448,582; Selden Co., British Pat. 281,742; *C.* (1928), II, 2213.

<sup>2</sup> A.E.G., German Pat. 401,485 (1923); Barringer und Peterson, U.S. Pat. 1,589,094.

<sup>3</sup> L. Weisberg and R. S. Potter, U.S. Pat. 1,424,137 (1922).

<sup>4</sup> Belgian Pat. 192,590 (1906).

<sup>5</sup> According to Griffith Bros. & Co. and R. P. L. Britton, British Pat. 269,973; *C.* (1928), II, 293, aromatic alcohols, such as benzyl alcohol and cinnamic alcohol, also yield resins with H<sub>2</sub>SO<sub>4</sub>, etc.

<sup>6</sup> U.S. Pat. 1,523,459; *C.* (1925), I, 2262.



alcohols, such as formalglycerine, formalglycol, glycerine-acetal, glycol-acetal, benzalglycerine, or benzal-glycol, in the presence of basic or acid condensing agents. The products so obtained are liquid, semi-solid, or hard plastic masses, according to the conditions maintained during the reaction, which resemble in properties the phenol-formaldehyde condensation products and may be used technically for similar purposes.

A resinous product may also be obtained from the oily by-product, consisting of alcohols and hydrocarbons, which is obtained in the catalytic reduction of carbon monoxide to methanol. The resin is produced by subjecting the by-product to the action of zinc chloride at high temperature and pressure.<sup>1</sup>

Complicated resins of an oxidizable character are obtained from  $\alpha$ - and  $\beta$ -naphthol and cyclohexanol in the presence of zinc chloride.<sup>2</sup> Crystallizable cyclohexyl-naphthols can be identified in the product.

## CONDENSATIONS WITH ACIDS

**Condensations with Hydroxyacids.** Aliphatic  $\beta$ -hydroxyacids and aromatic o-hydroxyacids possess the property of being easily transformed into cyclic anhydrides (lactides, salicylides). By the choice of suitable conditions or use of suitable condensing agents the reaction can easily be so conducted that mixtures of resinous character are formed.

Thus, E. Zimmermann<sup>3</sup> obtained a resin by heating lactic acid in a current of dry air or in a vacuum. At 100–150° C. a residue remains which deliquesces in the air, and which, on continuing to heat up to 150–200° C., is finally transformed into a hard substance, which, however, is still somewhat hygroscopic.

Regarding the improvement in the properties of this product by treatment with formaldehyde, see page 177.

On the other hand, the resins obtained by heating salicylic

<sup>1</sup> Bad. Anilin- u. Soda-Fabrik, German Pat. 419,912 (1923); French Pat. 586,031 (1924); *C.* (1926), I, 1057.

<sup>2</sup> Burchard, Alberti, *Ann.*, 450, 304 (1926); *C.* (1927), I, 1160.

<sup>3</sup> German Pat. 305,775.

acid or the cresotic acids (p-hydroxy-derivatives), or mixtures of these with acid condensing agents, such as phosphorus oxychloride, acetyl chloride, acetic anhydride, phosgene, thionyl chloride, and so forth, are directly utilizable, being stable to water.<sup>1</sup> Their solubility in numerous diverse solvents is remarkable; they are not only soluble in acetone, but also in aromatic hydrocarbons, turpentine oil, tetraline, and even in linseed oil. This circumstance, together with satisfactory fastness to light and to air, seems to indicate the suitability of these resins as materials for varnish manufacture.

Substances similar to shellac can also be produced by the condensation of aliphatic or hydroaromatic hydroxy-acids. If suitable components are used, products are obtained which are both soluble in alkalies and capable of being hardened.<sup>2</sup>

**Condensates from Acids and Naphthalene.** Whilst carboxylic acids show no special tendency to combine with hydrocarbons in general, naphthalene shows an appreciable tendency to combine with a few such acids. The process which takes place presumably consists in the formation of a ketone, as benzoic acid and benzene react to form benzophenone,<sup>3</sup> and succinic anhydride forms ketobutyric acids with such hydrocarbons as fluorene, anthracene, acenaphthene, dihydroanthracene, and so forth.<sup>4</sup>

Thus a shellac-like product is obtained from naphthalene and glycollic acid or glycollicides,<sup>5</sup> for example, by heating 120 parts of naphthalene with 40 parts of glycollic acid in the presence of 10 parts of phosphorus pentoxide under pressure to 130–170° C. for about 15 hours. Carbon dioxide and carbon monoxide are formed as by-products. The reaction mixture is

<sup>1</sup> Farbw. vorm. Meister, Lucius & Brüning, German Pat. 344,034 (1920); *C.* (1922), II, 580. On the other hand, the salicylides obtained in a similar manner from pure raw materials, which are also of amorphous or resinous character, and which have been known for a long time, show a limited solubility only; see Gerhardt, *Ann.* 87, 159 (1853); Schröder, Prinzhorn and Kraut, *Ann.*, 150, 1 (1869); *Ann.*, 163, 219 (1872); 245, 43 (1888); *Ber.* 34, 2951 (1901); 35, 3644 (1902); German Pat. 211,403.

<sup>2</sup> Siemens & Halske A. G., German Pat. 449,275.

<sup>3</sup> M. Kollarits and V. Merz, *Ber.*, 5, 447 (1872); 6, 536 (1873).

<sup>4</sup> German Pat. 376,635 (1921); *C.* (1924), I, 966; U.S. Pat. 1,547,280 (1921); *C.* (1925); II, 2298.

<sup>5</sup> Elektrochem. Werke G.m.b.H. (H. Bosshard and D. Strauss), German Pat. 354,864; *C.* (1922), IV, 397; British Pat. 171,956; *C.* (1922), II, 769.

freed from unchanged naphthalene by steam distillation, and then forms a brown resin which softens at 80–85° C. The phosphorus pentoxide may be replaced by phosphoric acid or by aluminium chloride.

A similar formation of resin occurs on interacting naphthalene with oxalic acid<sup>1</sup> in presence of acid condensing agents ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ).

Apart from naphthalene, halogenated naphthalenes may be caused to interact with glycollic or oxalic acid, either concentrated sulphuric acid or those substances already mentioned being used as condensing agents.<sup>2</sup>

It should be noted that the various products are insoluble in alkalis, which interferes with their use as shellac substitutes.

### CONDENSATION WITH ELIMINATION OF HALOGEN HYDRIDE

Although from a theoretical standpoint condensations with elimination of halogen hydride are almost as important as those in which water is eliminated, they are of limited application only for the production of synthetic resins. The reason is not that the reactions involved take place with more difficulty. Apart from the fact that the raw materials are usually more expensive, the formation of large quantities of acid halogen compounds, which are often removable with difficulty or not at all, is a great disadvantage, for apart from other difficulties and inconveniences, such as the necessity for complete absorption of the halogen compounds, and the use of acid-proof apparatus, there is always the danger that injurious amounts of acid constituents may remain in the resins, or be formed by subsequent elimination, which would then lead to difficulties such as the corrosion of metals, and so forth.

In condensation with elimination of water the formation of ethylene linkages can frequently be anticipated, and imparts to the products a more or less pronounced tendency to polymerization. This does not generally occur in the products of condensation with elimination of halogen hydride. It is true

<sup>1</sup> Elektrochemische Werke G.m.b.H. (H. Bosshard and D. Strauss), German Pat. 380,577; *C.* (1924), I, 1715.  
38,256; *C.* (1924), II, 1412.

that unsaturated compounds, which may possess polymerizing capacity, are formed, for example, by methylene chloride, and more generally by dihalogenides of the formula  $R \cdot CHX_2$ , but the use of such halogen derivatives in place of the aldehydes (for example, of methylene chloride instead of formaldehyde) offers no advantage and is, in addition, far too dear. The remaining halogen compounds which are possible for the production of resins all yield products which are not polymerizable; consequently the processes here to be discussed always yield resins which remain permanently soluble and fusible.

Condensations of this character occur with special facility if halogenated fatty-aromatic or aromatic compounds are used as raw materials. The reaction usually requires the use of suitable condensing agents, which include alkalis, metals (Zincke's synthesis)<sup>1</sup>, aluminium chloride (Friedel-Crafts'<sup>2</sup> synthesis), ferric chloride, zinc chloride, phosphorus oxychloride, and cuprous chloride.<sup>3</sup> The reaction proceeds in the well-known manner, according to which, for example, halogen alkyl and benzene form an alkyl-benzene. More than one hydrogen atom of the benzene reacts, and it is possible without difficulty to replace all six hydrogen atoms of benzene by alkyl. In the case of less highly substituted products, mixtures of positional isomers or homologues are frequently produced (in the o- and p-position), the products first obtained entering further into reaction. In addition the catalyst acts not only as a condensing agent, but also by promoting the elimination of alkyl groups.<sup>4</sup> This latter reaction occurs simultaneously, especially when small amounts only of aluminium chloride, for example, are used for condensations carried out at high temperatures, as is almost always the case in the manufacture of synthetic resins by such processes.<sup>5</sup> For purely synthetic reactions, molecular proportions of aluminium chloride are required.

<sup>1</sup> Th. Zincke, *Ann.*, 161, 93 (1872); 159, 373 (1871).

<sup>2</sup> Friedel, J. M. Crafts, *Compt. rend.* 84, 1392, 1459 (1877); *Ber.*, 10, 1180 (1877).

<sup>3</sup> J. Houben, *Arbeitsmethoden*, II, 808 (1925).

<sup>4</sup> F. Reindel, F. Siegel, *Ber.*, 56, 1551 (1923).

<sup>5</sup> G. Schroeter and associates, *Ber.* 57, 1990 (1924); on the theory of the Friedel-Crafts synthesis, see the recent articles by H. Wieland, L. Bettag, *Ber.*, 55, 2246 (1922); A. Schaarschmidt, *Angew.*, 37, 286 (1924).

As will be seen from the various possibilities of reaction which we have just described, all the conditions are present for the production of products in a resinous condition, if the conditions of reaction are suitably chosen. In practice, more or less considerable quantities of uncrystallizable impurities are often obtained in the course of ordinary scientific syntheses, employing these reactions.

For practical resin production by condensation with elimination of halogen hydrides, the following two classes of reaction are used—

(a) Reactions of halogenated hydrocarbons with one another or with non-halogenated products (hydrocarbons);

(b) Reactions of halogenated products containing oxygen, with one another, or the action of halogenated compounds on substances containing oxygen.

According to reactions (a), therefore, mixtures of hydrocarbons are obtained (which still contain minute amounts of halogen), and according to reactions (b) products which still contain oxygen.

**Hydrocarbon-resin Mixtures.** It must first be noted that the tendency to autocondensation of benzyl chloride under the influence of suitable reagents (for example, aluminium chloride), which has long been known, and which leads to the production of products of high molecular weight<sup>1</sup> has been exploited technically. The condensations between chloronaphthalenes, halogen addition products of hydrogenated naphthalenes and chloro-derivatives of p-cymol<sup>2</sup> presumably proceed in an essentially similar manner.

For example, 100 parts of benzyl chloride are mixed with 0.5 parts of anhydrous ferric chloride. The reaction takes place on standing for some time in the cold, with evolution of hydrochloric acid, and leads to the formation of a dark-brown, porous, solid mass, which is purified by treatment with steam, then ground, and finally washed with hydrochloric acid in order to remove the iron. The resin so produced has a yellowish

<sup>1</sup> J. Böeseken, *Ber. Ref.* 23, 98; *C.* (1904), I, 1135; Zinke, *Ber.* 2, 739 (1869); Onufrowicz, *Ber.*, 17, 833 (1884); Prost, *Ber.*, 19, 875 (1886); Radziewanowski, *Ber.*, 28, 1135 (1895); Nef, *Ann.*, 298, 248 (1897).

<sup>2</sup> P. H. Groggins, *Ind. Eng. Chem.*, 20, 1130 (1928).

colour and dissolves in benzene, carbon tetrachloride, chloroform, cyclohexanol and cyclohexanol acetate, but not in alcohol. The varnishes which may be obtained with such solvents form films which are very resistant to acids and alkalies, for example, to warm caustic soda solution of 40° Be.

o-chlorobenzylchloride and chloromethylnaphthalene may be used instead of benzyl chloride (or bromide). Ferric chloride may be replaced by the chlorides of aluminium or zinc, but the reaction then requires the application of heat.<sup>1</sup>

Technical chloronaphthalene mixtures are converted into a rosin substitute by melting and heating to 215° C., together with iron or other metallic catalysts, in a current of air or inert gases, by which means the constituents of low boiling point are removed.<sup>2</sup>

Resins are also obtained by heating the halogen addition products of crude anthracene and phenanthrene, to which aldehydes may be added, in the presence of condensing agents.<sup>3</sup>

Resins are obtained by the action of metallic halides ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ) on the halogen addition products of naphthalene or its derivatives, or from the halogen derivatives of hydrogenated naphthalenes, alone or in admixture with aromatic hydrocarbons. Condensation occurs in the presence or absence of a solvent. For example, 256 parts naphthalene are chlorinated in solution in 800 parts chloroform, and 20 parts of aluminium chloride are added to the crude mixture, containing the di- and tetra-chloride, after which this is boiled for several hours. After removing the solvent by steam distillation the temperature is considerably raised, by which means transparent, brittle resins are obtained, which are soluble in benzene, oil of turpentine, and linseed oil, but insoluble in alcohol.<sup>4</sup>

Viscous or resinous products can be obtained from halogen

<sup>1</sup> Bad. Anilin-u. Soda-Fabrik, German Pat. 280,377 (1913); 280,595 (1913); *Kunstst.*, 4, 392 (1914); 5, 8 (1915); *C.* (1915), I, 71; *Chem.-Ztg. Rep.* (1914), 573; see also German Pat. 326,729.

<sup>2</sup> Deutsche Conservierungsges. m.b.H., German Pats. 327,704 (1917); 332,725 (1920); *C.* (1921), II, 130, 743; *Kunstst.*, 11, 6 (1921); U.S. Pat. 1,455,509; *C.* (1924), I, 1716.

<sup>3</sup> Bakelite Ges.m.b.H. and M. Florenz, German Pat. 420,443 (1922); *C.* (1926), I, 2253.

<sup>4</sup> Aktien-Ges. f. Anilin-Fabr., German Pat. 332,391 (1918); *C.* (1921), II, 652; *Kunstst.*, 11, 94.

compounds containing the atomic grouping  $(R) \cdot (R_1) : CH \cdot X$ , in the presence of surface catalysts, such as fuller's earth or kieselguhr at temperatures below  $180^\circ C$ . The reaction may, if desired, be effected under pressure or in the presence of a solvent. Oils of all degrees of viscosity and resins of varying hardness may be obtained, according to the character of the raw materials and the other conditions, such as dilution with solvents. Thus, on heating *ac.*-1.2-dibromotetrahydronaphthalene to  $100^\circ C$ . in the presence of aluminium magnesium silicate, a resin is obtained which is soluble in most organic solvents.<sup>1</sup> Among other suitable halogen derivatives, pinene hydrochloride and the mixture of aliphatic halogenides obtained by chlorinating solar oil in the cold are included. Very probably free residues,  $(R) \cdot (R_1) : C :$  are produced by the elimination of halogen hydride and lead to immediate polymerization.

Further processes of this character result from the interaction of a hydrocarbon with a chlorinated hydrocarbon.

Whereas oily products are obtained by the condensation of naphthalene and its derivatives with aralkyl halides, such as benzyl chloride, solid, resinous condensation products are obtained on using more highly halogenated derivatives of benzene homologues, such as xylylene dichloride. Small amounts of iron or iron compounds, aluminium powder and bronze powder act as catalysts in this reaction.<sup>2</sup> The products are intended for purposes of impregnation,<sup>3</sup> or for the production of plastic masses together with cellulose derivatives.<sup>4</sup>

Aralkyl halides may also be condensed with polynuclear aromatic hydrocarbons or their halogen derivatives, with formation of oily or of solid resinous products in the absence of catalysts,<sup>5</sup> or in presence of hydrochloric acid gas.<sup>6</sup> The

<sup>1</sup> Chemische Fabrik auf Aktien (vorm. E. Schering), E. Freund, H. Jordan, German Pat. 417,667 (1921); *C.* (1925), II, 2102; *Kunstst.*, 16, 57 (1926).

<sup>2</sup> Farbenfabr. vorm. Fr. Bayer & Co., German Pats. 301,713 (1916); 302,521 (1916); *C.* (1921), II, 326; (1921), IV, 619; *Kunstst.*, 11, 29 (1921); see also German Pat. 302,531.

<sup>3</sup> German Pat. 302,531 (1917); *Kunstst.*, 11, 38 (1921).

<sup>4</sup> German Pat. 336,476 (1918); *Kunstst.*, 11, 190 (1921).

<sup>5</sup> Farb. vorm. Meister, Lucius & Brünig, German Pat. 416,904 (1920); *C.* (1925), II, 2101; *Kunstst.* 16, 56 (1926).

<sup>6</sup> Farb. vorm. Meister, Lucius & Brünig, German Pat. 417,442 (1920); *C.* (1926), I, 508.

oily products can be converted into solid resins by treatment with oxygen or air.<sup>1</sup> It is advantageous to carry out the reactions at a raised temperature, in the presence or absence of catalysts, such as  $\text{MnO}_2$  or  $\text{FeCl}_3$ . For example, in this manner a brown resin, easily soluble in linseed oil, aromatic hydrocarbons and acetone, is obtained from the oily condensation product from naphthalene and benzyl chloride, by the action of air in the presence of manganese dioxide at 170–190° C. The resins are suitable for the production of weatherproof varnishes, also for insulating purposes in the electrical industry, and as additions to varnish oils. The products are considerably improved by treatment with formaldehyde or with reagents of similar action, in the presence of small amounts of zinc chloride, sulphuric acid or hydrochloric acid, so that they are suitable for use in the production of oil varnishes.<sup>2</sup> Products soluble in alkali, which are distinguished by very marked powers of froth formation, are obtained by the interaction of naphthalenesulphonic acids with benzyl chloride.<sup>3</sup>

On heating a mixture of equal parts of xylene and ethylene chloride to 100–150° C. in the presence of 2 to 3 per cent of aluminium chloride, oily products are first produced, with evolution of hydrochloric acid, which are converted into resins on further heating. These are purified by washing and steaming.<sup>4</sup>

Catalysts of large surface development, such as fullers' earth, franconite, tonsil, and so forth, are used by E. Freund and H. Jordan<sup>5</sup> for the condensation of compounds of the aromatic series, such as naphthalene, xylene and the phenols of low temperature tar, with organic halogen derivatives, such as naphthalene tetrachloride, acetylene tetrachloride and acetyl chloride, with formation of resinous products. These hydro-silicates are alleged to offer the advantage over those catalysts

<sup>1</sup> Farbw. vorm. Meister, Lucius & Brüning, German Pat. 400,312 (1922); *C.* (1925), I, 307; *Kunstst.*, 15, 84 (1925).

<sup>2</sup> I. G. Farbenind. A.-G., German Pat. 446,999; *C.* (1927), II, 1402.

<sup>3</sup> I. G. Farbenind. A.-G., German Pat. 436,881; see also Tetralin G.m.b.H., German Pat. 319,799.

<sup>4</sup> Badische Anilin.-u. Soda-Fabrik, German Pat. 326,729 (1918); *Kunstst.*, 10, 214 (1920).

<sup>5</sup> British Pat. 202,997 (1923); Chemische Fabrik auf Aktien (vorm. E. Schering); *C.* (1925), I, 1455; German Pat. 417,667–8.



ordinarily used, that they are easily separable from the products of reaction, and do not lead to the formation of discoloured resins which are unstable in the air. For example, a hard resin, soluble in carbon tetrachloride, acetone, ethyl acetate and benzene hydrocarbons, and insoluble in alcohol, which softens at 65° C., is obtained from naphthalene and naphthalene tetrachloride in presence of 0.1 per cent of fullers' earth at 60–120° C. The resin obtained with the phenols of low temperature tar is very soluble in alcohol.

**Formation of Oxygenated Products.** The oxygenated condensates here to be considered, differ mainly from the condensation products from hydrocarbons by their solubility relationships. Thus, the presence of phenolic hydroxyl groups is associated with solubility in alcohol and in alkali, as is shown, for example, by the instance of the product from low temperature tar phenols referred to in the final paragraph of the previous section.

On treatment with chlorine of phenols methylated in the nucleus, at temperatures above 100° C., or on heating the chlorinated phenols under reduced pressure, resins are obtained which are soluble in alcohol, acetone, ether, and alkalies. Products of this character containing a high percentage of chlorine, are soluble in benzene hydrocarbons only. The resins are used for the production of dark or black varnishes, and are strongly bactericidal.<sup>1</sup>

A brittle mass, soluble in alcohol, is also obtained by the action of halogen on wood tar.<sup>2</sup>

Resinous products are also obtained by the treatment of fats, oils, and waxes with chlorine.<sup>3</sup> The oxidized paraffins behave similarly, and are easily chlorinated in solution, with formation of highly elastic, but hard resins.<sup>4</sup>

Mixtures of phenols with halogenated naphthalene, or with halogenated hydrogenated naphthalenes or with derivatives of the same, are condensed under the influence of metallic halides

<sup>1</sup> Chem. Fabr. vorm. Weiler-ter Meer, German Pats. 355,173 (1920), 355,174 (1920); *C.* (1922), IV, 380; *Kunstst.*, 13, 21 (1923).

<sup>2</sup> Riedel, German Pat. 320,620 (1918); *C.* (1920), IV, 136.

<sup>3</sup> Boehringer & Söhne, German Pats. 256,856, 258,156.

<sup>4</sup> I. G. Farbenind. A.-G., German Pat. 451,116.

( $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ) in the presence or absence of a solvent, forming resins which are not only soluble in benzene, chloroform, linseed oil, and oil of turpentine, but also in alcohol.<sup>1</sup> Thus, phenol is heated to  $100^\circ \text{C}$ . with a solution of tetrachloronaphthalene in tetrachlorethane in the presence of ferric chloride.

If phenols alone are used, aralkylphenols are obtained by interaction with aralkyl halides, which interact with formaldehyde, and so forth, in the same manner as the original phenols. The product obtained from commercial cresol and chlorobenzyl chloride is soluble in linseed oil, and its solution in that solvent can be converted into a resin which can be hardened, for example, by hexamethylene tetramine.<sup>2</sup>

Oily or soft condensation products are obtained, by heating in the absence of catalysts, from benzene derivatives halogenated in the side chain (benzyl chloride) and aromatic hydroxy-compounds (phenols).<sup>3</sup> On warming with phenols in the presence of small quantities of metallic halides ( $\text{ZnCl}_2$ ,  $\text{AlCl}_3$ ), aromatic hydrocarbons replaced by more than one halogen atom in the side chain, of the type  $\text{Ar} \cdot \text{CHX}_2$ , eliminate halogen hydride with formation of resins, which are very soluble in caustic alkalies, alcohols, benzene, toluene, and chloroform, but very slightly soluble in alkali carbonates.<sup>4</sup> The products correspond to those obtained from aldehydes and phenols.

Resinous or plastic products are obtained from compounds of the type  $(\text{R}) \cdot (\text{R}_1) : \text{CH} \cdot \text{X}$ , where R and  $\text{R}_1$  represent monovalent residues of any kind, in the presence of aldehydes, ketones, or phenols, by elimination of halogen hydride under the influence of suitable reagents such as fullers' earth. If formaldehyde or its derivatives are used, infusible substances are obtained. Other aldehydes, ketones, or phenols yield fusible products.<sup>5</sup>

<sup>1</sup> Akt.-Ges. f. Anilin-Fabrikation, German Pat. 334,710 (1918); *C.* (1921), II, 964; *Kunstst.*, 11, 94 (1921).

<sup>2</sup> I. G. Farbenind. A.-G., German Pat. 446,999.

<sup>3</sup> Kalle & Co., German Pat. 346,384 (1917); *C.* (1922), II, 1140.

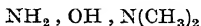
<sup>4</sup> Dynamit-A.-G. vorm. A. Nobel & Co., German Pat. 355,389 (1920); *C.* (1922), III, 441.

<sup>5</sup> Chemische Fabrik auf Aktien (vorm. E. Schering), E. Freund, H. Jordan, German Pat. 417,668 (1921); *C.* (1925), II, 2102.

The proposal has recently been made<sup>1</sup> to improve the properties of artificial oils and resins by treating them with aralkylhalides in the presence or absence of catalysts. The aralkyl residue enters the aromatic nucleus, leaving any available hydroxyl groups intact. The products show increased viscosities or higher softening points, improved fastness to light, and solubility in linseed oil or aromatic hydrocarbons. The following products may be treated in this manner: phenol-formaldehyde condensation products, phenol-sulphur resins, oily reaction products of xylene with formaldehyde, cumarone resin, naphthylamine-acetaldehyde resin, and so forth.

### CONDENSATIONS WITH FIXATION OF SULPHUR AND ELIMINATION OF HALOGEN HYDRIDE OR HYDROGEN SULPHIDE

As is well known, sulphur dyestuffs are formed on heating substances of the most varied character, usually aromatic, with reagents capable of supplying sulphur.<sup>2</sup> These dyestuffs are almost always mixtures of substances which mostly possess high molecular weight, and are distinguished by almost complete absence of any power of crystallization. Black, blue, red, yellow, or brown products are obtained, according to the character of the raw materials and the method in which the reaction was effected. The dyestuff character is associated with the presence of certain ring formations, such as thiazol (yellow and brown dyestuffs), thiazine (blue and black dyestuffs), azine (red dyestuffs), and so forth, and also with the presence of auxochromic groups, such as



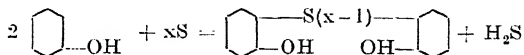
and so forth. The substances which have been found especially suitable for the production of such dyestuffs are p-dihydroxybenzenes, toluquinone, pyrocatechin, dihydroxynaphthalenes, naphtoquinone, amino- and aminohydroxy-benzenes and similar substances. On the other hand, the condensation products of phenol itself and of the hydrocarbons, which are equally

<sup>1</sup> I; G. Farbenind. A.-G., German Pat. 444,109; *C.* (1927), II, 750.

<sup>2</sup> Otto Lange, *Die Schwefelfarbstoffe*, 2, Aufl., Leipzig (1925).

easily prepared, show no dyestuff character.<sup>1</sup> Together with yellow and brown products they, therefore, serve as promising substitutes for resins and as plastic masses on account of their cheapness.

According to Möhlau,<sup>2</sup> the reaction between *phenol* and sulphur consists first in the entry of the mercaptan group in the *o*-position to the hydroxyl group, with formation of mercaptans, which then form polysulphides:



Thus, on heating phenol with sulphur to 100–115° C. until the evolution of hydrogen sulphide ceases, a mixture of yellowish to intensively yellow substances is obtained, which are insoluble in strong sulphuric acid and in organic solvents, excepting pyridine bases and phenol, and which are readily soluble in alkalis only. From this mixture of various ( $x$  to 8) sulphur-containing products the most stable can be isolated, namely, the well-known phenol-*o*-disulphide of Haitinger.<sup>3</sup> The sulphur present in the form of polysulphides is capable of further reaction, and links the various molecules together with further evolution of hydrogen sulphide. Under suitable conditions, such as high temperature, these processes continue until the whole of the available sulphur has been utilized and stable disulphide chains have been formed. Under given conditions of reaction, the tendency of the chains containing more sulphur to change to those containing less<sup>4</sup> continues until those compounds are formed which happen to be the most stable.

Apart from the formation of sulphur chains there is sometimes the possibility of ring formation, including mercaptan sulphur as one of the ring-forming elements (especially in cases in which dyestuffs are formed).

This latter tendency is particularly marked when sulphur

<sup>1</sup> German Pat. 123,612; Cresols from brown dyestuffs; German Pat. 102,897.

<sup>2</sup> *Chem.-Ztg.* (1907), 937; see G. Schultz, H. Beyschlag, *Ber.*, 42, 743, 753 (1909); B. Holmberg, *Ber.*, 43, 220, 226 (1910).

<sup>3</sup> *Monatsh.*, 4, 163 (1883).

<sup>4</sup> J. Bloch, F. Höhn, G. Bugge, *J. prakt. Chem.*, 82, 743 (1910); *Ber.*, 41, 1961, (1908).

chloride is used, which primarily forms sulphides with phenols, hydrocarbons, and so forth, with evolution of hydrochloric acid. Thus phenol and sulphur chloride form dihydroxydiphenyldisulphide. On the formation of  $\beta$ -naphthol sulphide from  $\beta$ -naphthol and sulphur chloride and its conversion into naphthoxine, see, for example, Lesser and Gad;<sup>1</sup> on the formation of thianthrene derivatives and their disulphides by the interaction between p-xylene or guaiacol and sulphur chloride, see Monmohan Sen and Inanendra Nath Ray.<sup>2</sup>

It seems to follow from the whole character of the reaction that when sulphur chloride is used the primary products of the reaction are able to interact further in the same manner, not only with ring formation, but also with chain formation and increase of molecular magnitude. Apart from the formation of disulphides, partial chlorination may also occur.

As may be deduced from the reactions described above, the conditions for resin production are present if the reaction is suitably carried out. The conversion of the raw materials into insoluble masses, which may be capable of being hardened, is dependent on the presence of suitable quantities of sulphur or sulphur chloride; the storage of sulphur in the primary products in the form of polysulphides appears to be characteristic of these conditions. The solubility of the products is greatly influenced by the proportion of sulphur in the reaction mixture.

**Condensation of Phenols with Sulphur.** The production of artificial resins from phenols and sulphur has been especially developed by the Gesellschaft für chemische Industrie, of Basle. It was found that the melting point and degree of hardness of the resulting resins increased with the quantity of sulphur used, whilst their solubility in the usual solvents was simultaneously diminished. The condensation of phenols with sulphur is effected by heating in the presence of basic materials, to which accelerators may be added, consisting of halogens or halogen compounds. Heating is continued until the evolution of hydrogen sulphide ceases. The most various

<sup>1</sup> *Ber.*, 58, 2551 (1925); 56, 963 (1923).

<sup>2</sup> *C.* (1922), I, 818; (1926), II, 893.

basic substances are used, such as inorganic hydroxides, hydrosulphides, carbonates, acetates, aromatic amines, and so forth.<sup>1</sup>

The resins which are so produced are odourless, strongly adhesive, and light coloured in a thin layer only. They are very soluble in alkalis, alcohol, ether, acetone, and benzene, but insoluble in aliphatic hydrocarbons and their halogen derivatives and in acids. On further heating, with or without pressure, these resins are converted into infusible products which are insoluble in the ordinary solvents. The same effect can be achieved even better by similar treatment after the addition of sulphur, formaldehyde, hexamethylenetetramine, and so forth. From these properties the utility of these condensation products for the manufacture of varnishes and moulded articles is obvious. When they are used for the production of casts, that is, in the molten form, without solvents, the addition of considerable quantities of amines or amine resins as fillers is recommended.

The phenols which are used comprise phenol itself, its homologues and substitution products,  $\alpha$ -naphthol,  $\beta$ -naphthol, pyrocatechin, resorcin and pyrogallol.<sup>2</sup> The products from polyvalent phenols are distinguished by peculiar solubility, being insoluble in benzene hydrocarbons, but more or less soluble in water. In other respects, they behave in a similar manner to the resins from monovalent phenols.

As an example of the method of operation, a mixture of 47 parts phenol and 32 parts sulphur is melted in an apparatus provided with a reflux condenser; 1 part of potassium hydrosulphide is then added and the mixture heated to 130–140°C. The reaction, which is effected at a gradually rising temperature, is finished when the evolution of hydrogen sulphide ceases. A viscous, liquid resin is obtained, which solidifies on cooling

<sup>1</sup> German Pat. 400,242 (1920); *C.* (1925), I, 1261; see also Dutch Pat. 7,538; *C.* (1923), II, 337; German Pat. 379,003.

<sup>2</sup> *Ges. für chem. Industrie*, French Pat. 537,207 (1921); *C.* (1922), IV, 894; British Pat. 186,107 (1921); *C.* (1923), II, 256; U.S. Pat. 1,435,801 (1922); Blumfeldt, *Kunstst.*, 14, 42 (1924); Swiss Pats. 92,408; *C.* (1922), IV, 1088; 94,801, 95,186–7, 95,328–9; *C.* (1923), II, 411; 104,015; *C.* (1924), II, 1280; 105,855–105,858; *C.* (1926), I, 251. On the use of the acid oils from high and low temperature tars, see C. Ellis, U.S. Pat. 1,636,596; *C.* (1928), II, 294.

and which is soluble. On further heating to 150–180° C., the resin is converted into the infusible and insoluble form.

Derivatives of the above-mentioned resins have been obtained by treatment with acylating agents such as p-toluenesulphochloride,<sup>1</sup> by which means the free phenol-hydroxyl groups are caused to interact with the acid residues, resulting in deep-seated changes in the solubility relationships. The esters, which are also pale yellow to brownish yellow resins, are no longer soluble in alcohol or in alkalis; they are, however, soluble in chloroform, ethylene chloride, mixtures of aliphatic and halogenated or hydrogenized aromatic hydrocarbons, and in a mixture of acetone and alcohol. With the help of suitable solvents, such as benzyl alcohol and cyclohexanol, they can be incorporated not only with linseed oil (to form linseed oil varnishes), but also with cellulose esters and with rubber, and can thus be utilized for very varied purposes.

A further improvement of the properties of the resins obtained by the action of sulphur on phenols, containing 20 to 25 per cent of sulphur, is alleged to be effected by treatment with inorganic or organic bases, such as cyclohexylamine, which may be carried out in the presence of diluents or solvents, and may also be combined with the action of formaldehyde. The resinous products so obtained, which may be further improved by the addition of substances to confer elasticity, such as beeswax, and so forth, resemble natural shellac and are, therefore, especially intended for use in polishes. The covering power, fastness to light, and lustre of the polish are stated to be equal to those of natural shellac. The colour of the new resins is the same as that of bleached shellac, but they are stated to be still harder.<sup>2</sup>

**Condensation of Aromatic Amines with Sulphur.** Primary and secondary aromatic amines, with the exception of p-toluidine

<sup>1</sup> Ges. f. chem. Industrie in Basel, French Pat. 568,840 (1923); British Pat. 203,310 (1923); Swiss Pats. 103,432 (1922); 103,244–103,247 (1922); *C.* (1924), II, 1280; 106,471–106,473; 109,651–109,657; German Pat. 418,498 (1923); *C.* (1926), I, 251.

<sup>2</sup> Ges. f. chem. Ind., Basel, German Pat. 431,599 (1923); British Pat. 221,205 (1924); French Pat. 585,379 (1924); Austrian Pat. 103,227 (1924); Swiss Pat. 107,626 (1923); *C.* (1926), II, 1466; *Kunstst.* 16, 254 (1926); *Farbe und Lack* (1927), 286.

and the N-alkylated anilines, form resinous condensation products when heated with a quantity of sulphur larger than that required to form the monosulphides.<sup>1</sup> The reaction may be effected in the presence of catalysts such as iodine. The resins are soluble in acetone, but more or less insoluble in alcohol, benzene, and so forth. On using more sulphur than is required for the production of the products just referred to, more or less insoluble products are formed, which are hardened by further heating. Whilst 1 molecule aniline and 2 molecules sulphur, on heating for 32 hours to 185–220° C. form a pale yellow, soluble resin, which softens above 15° C., on heating 1 molecule aniline and 3 molecules sulphur for 21 hours to 185–250° C. a yellowish brown product is obtained, which softens at above 100° C. and is no longer completely soluble in acetone, and which becomes quite insoluble and infusible on further heating. The sulphur contents of the resin first described are 36.5 per cent, and those of the second 44.08 per cent.

**Condensation of Various Substances with Sulphur.** F. Hassler<sup>2</sup> produces condensation products from aromatic hydrocarbons and sulphur, which are intended for use as resin substitutes. A resin-like product is also obtained from phenyl sulphide and sulphur on prolonged heating.<sup>3</sup> A substance used for impregnating, and known as Toron, is produced in America from turpentine oil and sulphur.<sup>4</sup> It is very soluble in hydrocarbons, and is probably similar in many respects to factis, which is also produced by the action of sulphur. Sulphur is also used, not only for the vulcanization of rubber and similar products, but also for producing a similar effect on numerous artificial products, a subject which we are unable to discuss here.

<sup>1</sup> Ges. f. chem. Industrie in Basel, German Pat. 401,168 (1923); Swiss Pats. 104,567; 104,933–104,935; *C.* (1925), I, 308; U.S. Pat. 1,654,856; *C.* (1928), I, 1809.

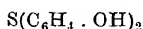
<sup>2</sup> German Pat. 409,713 (1920); *C.* (1925), I, 2730; German Pat. 407,994. On products from anthracene oil and sulphur, see German Pat. 330,970 (1919); *Kunstst.*, II, 55 (1921); German Pat. 332,888 (1919); on products from unsaturated hydrocarbons and sulphur or  $S_2Cl_2$ , see Gardner, U.S. Pat. 1,446,039; *Kunstst.* 15, 26 (1925); from phenol, naphthalene, anthracene, and so forth, or mixtures of these, with sulphur and  $S_2Cl_2$  see Cutler-Hammer Mfg. Co., U.S. Pat. 1,616,741; *C.* (1928), II, 497.

<sup>3</sup> Krafft, Lyons, *Ber.*, 29, 436 (1896).

<sup>4</sup> Pratt, U.S. Pat. 1,349,909 (1920); C. Ellis, *Synthetic Resins*, 317.



**Condensation of Phenols with Sulphur Chlorides.** Both sulphur monochloride,  $S_2Cl_2$ , and sulphur dichloride,  $SCl_2$ , react very easily with phenols, with liberation of hydrogen chloride and formation of resins containing sulphur. As early as 1887, Tassinari<sup>1</sup> observed that in the reaction between phenols and sulphur dichloride, which is conveniently effected with reduced violence by the use of a diluent, such as carbon disulphide, resinous products of the character of disulphides are produced in addition to dihydroxydiphenylsulphide,



Apart from phenol, such resins were formed by p-bromophenol, trichlorophenol, the nitrophenols, o- and p-cresol and thymol, slowly by  $\beta$ -naphthol, but very easily by  $\alpha$ -naphthol.

Recent investigations of these resins were carried out by C. Ellis,<sup>2</sup> who found that the properties of the resins were very greatly dependent on the proportion of sulphur chloride which was used. The larger the proportion of sulphur monochloride ( $S_2Cl_2$ ) to phenol, the harder, more infusible and less soluble were the resultant resins. It was also found that for the production of a resin of a definite hardness, solubility, and so forth, phenol required considerably more sulphur chloride than cresol. Whilst the resins with a lesser proportion of sulphur are soluble in alcohol, benzene, acetone, sulphur, phenol, aniline and aqueous solutions of caustic alkali, with increasing proportions of sulphur the solubility in alcohol, benzene, and acetone gradually disappears, and the products are soluble in sulphur, phenol, aniline and caustic alkali solutions only. If the proportion of sulphur chloride is increased to 350 per cent, products are obtained containing 60 per cent of sulphur, which are practically unattackable.<sup>3</sup>

The production of a resin soluble in alcohol is carried out approximately as follows:<sup>4</sup> p-cresol, for example, is dissolved in toluene, and sulphur monochloride,  $S_2Cl_2$ , is gradually added

<sup>1</sup> *Gaz. chim. Ital.*, 17, 83, 90 (1887).

<sup>2</sup> *Synthetic Resins*, p. 311.

<sup>3</sup> C. Ellis, U.S. Pat., 1,663,160; *C.* (1928), II, 816.

<sup>4</sup> C. Ellis, U.S. Pat. 1,564,002 (1922); *C.* (1926), I, 2628.

to the amount of  $1\frac{1}{2}$  times the weight of the cresol. After the evolution of hydrochloric acid has ceased the solution is maintained at  $150^{\circ}\text{C.}$ , whilst air is blown through it for half an hour, by which means the remaining hydrochloric acid, the toluene, and any traces of evil-smelling chlorophenols or similar substances are removed. The resin dissolves easily in methylated spirits with a dark-brown colour. By adding syrupy phosphoric acid to the alcoholic solution the colour is changed to pale yellow. The alcoholic solution of the resin is used for the production of acid-proof coatings, on wood for example, which are unattacked even by fuming sulphuric acid. It can be dyed by all classes of dyestuffs.

A similar product has also been proposed for the manufacture of oil varnishes.<sup>1</sup>

By the simultaneous action of sulphur halides and acylating agents on phenols and naphthols, with or without the presence of water, aqueous alkalis or other solvents or diluents, sulphur-containing esterified resins are obtained, which are completely identical with those obtained by condensation with sulphur.<sup>2</sup>

Certain derivatives or transformation products of the condensation products obtained from sulphur chlorides and phenols are used as mordants in dyeing and also in tanning.<sup>3</sup>

**Condensation of various Substances with Sulphur Chlorides.** Resins obtained from aniline and toluidine with sulphur monochloride were investigated by C. Ellis.<sup>4</sup> With sufficient

<sup>1</sup> C. Ellis, U.S. Pat. 1,557,519 (1921); *C.* (1926), I, 1301.

On its use as a plastic mass, with the addition of small amounts of stearin pitch (preferably in the form of a solution), see Cutler-Hammer Mfg. Co. and G. J. Votapek, U.S. Pat. 1,574,771; *C.* (1926), I, 113.

<sup>2</sup> Ges. f. chem. Industrie in Basel, German Pat. 425,798 (1924); Swiss Pats. 109,068; 109,651-109,657 (1923); *C.* (1926), I, 2853; French Pat. 568,840; *C.* (1924), II, 1280; U.S. Pat. 1,588,439; *C.* (1927), I, 190.

<sup>3</sup> German Pats. 389,360, 406,675, 436,523, 437,977; *C.* (1924), II, 762; (1925), I, 1670; (1927), I, 188, 3229; British Pats. 232,958, 242,974, 248,007; *C.* (1926), I, 3944; II, 2945; (1927), I, 3229; French Pat. 596,301, and patent of addition, 30,997; *C.* (1926), I, 3949; (1927), I, 3229; U.S. Pat. 1,553,014; *C.* (1926), I, 508.

<sup>4</sup> *Synthetic Resins*, p. 314; includes bibliography. On nature of reaction, see Claus and Krall, *Ber.*, 4, 99 (1871); Smith, *Ber.*, 8, 1445 (1875); Schmidt, *Ber.*, 9, 1050 (1876); 11, 1168 (1878); Hanemann, *Ber.*, 10, 403 (1877); 12, 681 (1879); Holzmann, *Ber.*, 19, 1570 (1886); 21, 1636, 2063 (1888); Kym, *Ber.*, 21, 2807 (1888); 23, 2458 (1890); Michaelis, *Ber.*, 28, 165 (1895); Neik, *J. Chem. Soc. Trans.*, 119, 1166 (1921); Coffey, *Rec. trav. chim.* 40, 747 (1921).

proportions of sulphur chloride, brittle, insoluble resins were obtained, but the products do not offer any opportunity for technical exploitation.

Resin-like and rubber-like substances can be obtained by the action of sulphur monochloride or of selenium chlorides on aromatic hydrocarbons in the presence of metals or metallic chlorides, if vigorous action is promoted either by the use of large proportions of sulphur chloride, or by increased application of heat, or by prolonged duration of the process.<sup>1</sup> The nature of the catalyst is of special importance. Thus, from benzene and sulphur monochloride, in presence of iron or ferric chloride, a swollen, rubber-like, insoluble substance is obtained. In presence of aluminium chloride resins are formed, which are very soluble in benzene and other organic solvents, and which are converted by the further action of sulphur chloride into substances soluble in carbon disulphide only, and finally into products which merely gelatinize without dissolving. It is not stated to what extent sulphur is combined in this reaction, or whether the processes which take place are mainly of a chlorinating character, followed by condensations.

The well-known processes of factis manufacture and the vulcanization of rubber are also condensations with sulphur chloride, in which the raw materials are mainly natural products, such as fatty oils or india-rubber. Corresponding treatments are also imparted to artificial resins such as anhydroformaldehyde aniline,<sup>2</sup> cumarone resin,<sup>3</sup> aldehyde resin,<sup>4</sup> polymerides of vinyl-derivatives,<sup>5</sup> and so forth.

**Condensation with Liberation of Hydrogen (Oxidation).** Resinous condensation products are obtained by the oxidation of aromatic hydrocarbons, and especially of phenols, under suitable conditions. The essential resin-forming reactions are

<sup>1</sup> Dubois, Kaufmann. German Pat. 372,664; *C.* (1923), IV, 600.

<sup>2</sup> Böhler, German Pat. 317,267 (1918); *C.* (1920), II, 340; *Kunstst.*, 10, 21, 150, 215 (1920); German Pat. 335,984; *Kunstst.*, 11, 118, 142 (1921).

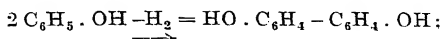
<sup>3</sup> Lender, German Pat. 277,605 (1913); *C.* (1914), II, 742; *Kunstst.*, 4, 35 (1914); Dutch Pat. 138 (1914); *Angew.*, 27, 11 (1914); Schlatter, U.S. Pat. 1,294,838 (1919).

<sup>4</sup> Elektrizitätswerk, Lonza A.-G., Swiss Pat. 89,064 (1920); *Kunstst.*, 13, 45 (1923).

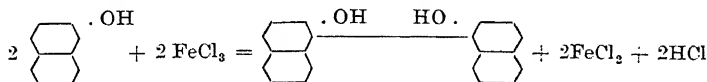
<sup>5</sup> Consortium f elektrochem. Ind., British Pat. 261,748; *C.* (1927), I, 1892.

probably nuclear condensations, which occur in a manner analogous to that of the following examples.

Phenol may be oxidized by permanganate to form p-di-phenol:<sup>1</sup>



$\beta$ -naphthol is oxidized with condensation by ferric chloride in aqueous<sup>2</sup> or ethereal<sup>3</sup> solution to form  $\beta$ -dinaphthol:



It is to be expected that, as in the corresponding pyrogenic condensations, considerably more than two molecules may be united to form a single complex. Another circumstance which may assist resinification is the possibility of various oxidation processes other than those leading to nuclear condensation. Thus it may be assumed that hydrocarbons are oxidized to phenols,<sup>4</sup> and also to quinonic compounds such as dipheno-quinones,<sup>5</sup> oxides, or peroxides,<sup>6</sup> and so forth, in addition to degradation products of lower molecular weight. The course of the reaction is naturally greatly dependent on the choice of oxidizing agent.<sup>7</sup>

Apart from nuclear condensation, condensation through two phenolic hydroxyl groups, with elimination of water, may also occur and may promote resin formation.

Three methods have been proposed for the production of resins from phenols by oxidation, which differ by the oxidizing agent used.

<sup>1</sup> A. P. Dianin, *J. prakt. Chem.* (1883), 875; *Ber.* 15, 1194 (1882); H. Goldstein, *Ber.*, 7, 734 (1874).

<sup>2</sup> A. P. Dianin, *Ber.*, 6, 1252 (1873).

<sup>3</sup> V. Merz, W. Weith, *Ber.*, 14, 2345, Footnote (1881); H. Walden, *Ber.*, 15, 2166 (1882); J. Houben, *Methoden*, II, 782 (1925).

<sup>4</sup> F. Fichter, *C.* (1924), II, 2832; Ono, *J. Chem. Soc., Japan*, 42, 38 (1921).

<sup>5</sup> K. v. Auwers and co-workers, *Ber.*, 38, 226 (1905); 41, 2332 (1908); 57, 1270 (1924).

<sup>6</sup> R. Pummerer and co-workers, *Ber.*, 58, 1808 (1925); 59, 2161 (1926).

<sup>7</sup> On electrochemical oxidation processes, see F. Fichter, *Trans. Amer. Electr. Soc.*, 45, 20; *C.* (1924), II, 2832; according to which phenols form nuclear condensation products with a sufficiently low current concentration only, forming various dihydroxydiphenyls and products of higher molecular weight which could not be identified.

According to F. Fischer,<sup>1</sup> resinous or bituminous substances are obtained from phenols, acid tars or tar oils by oxidation with oxygen, or with gases containing oxygen, at high pressure, for example, with air at 40 atmospheric pressure at 200° C. The process can be carried out in the presence of aqueous alkalis or acids, or in the presence of catalysts such as iron, or of diluents such as hydrocarbons. Thus, for example, from o-cresol in the presence of  $\text{NH}_2\text{SO}_4$  at 150° C., a hard orange-coloured resin was obtained, soluble in benzene and in alcohol, together with a brown product, insoluble in benzene, and small quantities of substances with dyeing properties. The latter are evidently fuchsine derivatives, which are formed by the condensation of cresol with aldehyde produced by oxidation.

Air or oxygen at the ordinary pressure has also a resinifying effect on cresols or xylenols<sup>2</sup> in the presence or absence of catalysts, such as manganese dioxide or ferric chloride. For example, a current of moist air is led through o-cresol for 10 to 12 hours at 150–170° C. in the presence of 0.2 per cent of manganese dioxide, after which unchanged cresol is removed by steam distillation. According to the duration of the treatment and the temperature, hard, dark-brown to black substances are obtained, which are soluble in ether, alcohol, acetone, benzene, and so forth, but insoluble in cold turpentine oil and in dilute sodium carbonate solutions.

Pummerer<sup>3</sup> obtained resinous products from phenols and homologous products by moderate oxidation with such substances as potassium ferricyanide or ferric chloride. By the action of alkalis, acids or heat the products so obtained either become soluble in alkali or are further polymerized. By reduction, colourless products are obtained, which can be converted into products insoluble in alkali by alkylation or acylation.

<sup>1</sup> British Pat. 149,979 (1920); *C.* (1921), II, 75; *Kunstst.* 11, 15 (1921); see also F. Fischer, Ehrhardt and Schrader, *Ges. Abhandlungen zur Kenntnis d. Kohle*, 4, 280, 293 (1919); *C.* (1921), II, 606; German Pat. 347,521.

<sup>2</sup> Chemische Werke Grenzach, A.-G.; German Pat. 357,756; *C.* (1922), IV, 956.

<sup>3</sup> British Pat. 165,408 (1921); *C.* (1921), IV, 1014; German Pat. 370,083; *C.* (1923), II, 1000; Swiss Pat. 98,315; *C.* (1923), IV, 670; Austrian Pat. 94,215; *C.* (1924), I, 2744; French Pat. 537,335.

The products yield viscous, colloidal solutions with benzene, ether, and so forth.

## VARIOUS RESIN-FORMING CONDENSATIONS

Resinifying processes occur in the course of innumerable condensation processes, usually as a mere auxiliary to the main reaction, which can, however, often be converted into the main process by suitable choice of the conditions of reaction. In the majority of cases this is, of course, of no practical importance, and, consequently, we will deal below with such reactions as do not belong to any of the classes already discussed, and the practical application of which for resin production has been proposed in the patent literature or elsewhere.

**Resin from Phenols and Thionyl Chloride.**  $\text{SO}_2\text{Cl}_2$ .<sup>1</sup> On condensing 2 molecules phenol with more than 1 molecule thionyl chloride in concentrated sulphuric acid, with cooling, resins of high melting point are obtained, which are soluble both in the usual aliphatic solvents, such as alcohol, and also in alkalies, even when dilute.

**Resins Produced with Aromatic Sulphochlorides.**<sup>2</sup> Salts of resinic acids (colophony), humic acids, lignoceric acid, or soft pitch, anthracene oil, and so forth, also products which contain phenolic substances, are caused to react with sulphochlorides, such as p-toluenesulphochloride, purified and dried. The resins so obtained have a high melting point, are stable to air and light, and are soluble in the ordinary solvents and also in hydrocarbons and in linseed oil.

**Resins from Phenols and Lead Oxide.**<sup>3</sup> The basic lead phenolates, which are easily prepared, can be obtained in amorphous form. They dissolve readily, in benzene for example,

<sup>1</sup> Farbw. vorm. Meister, Lucius & Brünig, German Pat. 362,383; *C.* (1923), II, 921.

<sup>2</sup> Melamid, German Pat. 380,825; Austrian Pat. 89,150; British Pats. 133,712-3 (1919); *Kunstst.*, 10, 68, 158 (1920); French Pats. 518,100-1; *C.* (1921), IV, 301, 1192; Swiss Pat. 91,567; Norwegian Pat. 32,166; p-toluenesulphochloride, obtained as a by-product of saccharine manufacture, is an especially cheap product, which has found many applications in the manufacture of synthetic resins; see W. Herzog, *Kunstst.*, 16, 105 (1926).

<sup>3</sup> F. Fischer, Ehrhardt, *Ges. Abhandl. zur Kenntnis der Kohle*, 4, 264; *C.* (1921), II, 854.

and might therefore be used as coatings, as rust preventatives. Their use for such purposes is open to the objection that they crystallize very readily, especially those obtained from phenols of low molecular weight.<sup>1</sup>

**Resin from Carbolic Oil or Creosote Oil.**<sup>2</sup> Resins are formed by treatment of carbolic oil or creosote oil with concentrated sulphuric acid.

**Resins from Phenols and Terpene Hydrocarbons.**<sup>3</sup> Oily and resinous condensation products are formed if phenols, especially naphthols, are treated in the presence of catalysts with terpene hydrocarbons, such as turpentine oil, ethereal oils, or unsaturated synthetic hydrocarbons of the general formula



The following catalysts may be used :



oxalic acid, sulphonic acids (especially p-toluenesulphonic acid),



silicates, such as Florida earth and fullers' earth, chlorine, bromine and iodine. The reaction results in the formation of phenoethers and terpenylphenols. The resinous products dissolve in hydrocarbons.

Resinous products soluble in benzene and in oils are obtained by the action of aldehydes on the condensation products of phenols and unsaturated hydrocarbons, such as terpenes, and so forth.<sup>4</sup>

**Resins from Hydrocarbons.** Certain hydrocarbons, such as

<sup>1</sup> On the use of naphthenates, such as zinc naphthenate, as paints and plastic masses, see German Pat. 383,815 (1921) of C. Jäger, G.m.b.H.; *Kunstst.*, 14, 28 (1924); *C.* (1924), I, 268.

<sup>2</sup> Chem. Fabriken Worms, A.-G., British Pat. 156,668 (1921); *C.* (1921), II, 808.

<sup>3</sup> H. Wuyts, French Pat. 539,494; *C.* (1923), IV, 951; *Kunstst.*, 13, 125 (1923); U.S. Pat. 1,469,709; *C.* (1924), I, 1717; German Pat. 396,106; *C.* (1924), II, 1028; also British Pat. 204,754; see also the investigations of W. Schrauth and K. Quasebarth (*Ber.* 57, 854; *C.* (1924), II., 326) on the condensation of cyclic hexenes with phenol.

<sup>4</sup> Bakelite Ges. m.b.H., German Pat. 340,989.

tetra- and deka-hydronaphthalene, show the property of rupture of the ring under the influence of alternating currents, followed by re-combination of the fission products. The products are subject to autoxidation, and the process must therefore be conducted in an atmosphere of nitrogen. They can be used as varnish oil substitutes.<sup>1</sup>

<sup>1</sup> Siemens & Halske, A.-G., and H. Becker, British Pat. 275,803; French Pat. 622,474.



## CHAPTER XI

### CUMARONE AND ALDEHYDE RESINS—THE COMMERCIAL- LY IMPORTANT SYNTHETIC RESINS

**Introduction.** Although, as will have been gathered from the preceding chapters, the number of possible methods of artificial resin production is extremely large, a few main processes are alone used at present in technical use. The reason is to be found in the fact that the profitable manufacture of artificial resins must be based on cheap raw materials, which are available in ample quantity. The number of possible raw materials is for this reason very limited. The quality of the products must also be satisfactory, and this is not easily achieved, but necessitates very careful development of the process in all its details, the results of which are, for the most part, naturally not published. An approximate idea of the very large amount of work which has been carried out may be gained by an inspection of the patent literature of the subject, but it must be remembered that patent specifications must not be judged by the same standards as ordinary scientific publications.

For these reasons the following descriptions must be recognized to be incomplete. Even the practical manufacturer only acquires special knowledge of all details in special cases, as it is impossible to investigate all the proposals and improvements in practice. On the other hand, questions of plant design, which are kept very secret, play a very important and sometimes a decisive part, as the general experience that laboratory and works results are two entirely different things, is nowhere more true than in artificial resin manufacture.

Although certain quantities of artificial resins are used which are manufactured by methods other than those described here (for example, glycerine-phthallic acid resins, sulphur resins, and so forth), it may be maintained that much more than 90 per cent of the ordinarily used products consist of: (1)

Cumarone resins, (2) Aldehyde resins, or (3) Phenol-formaldehyde resins, of which the Cumarone resins form the main portion, whilst the consumption of aldehyde resins is limited. These three classes of resins will first be discussed, and a discussion of (4), urea-formaldehyde condensates, the importance of which is rapidly increasing, will follow.

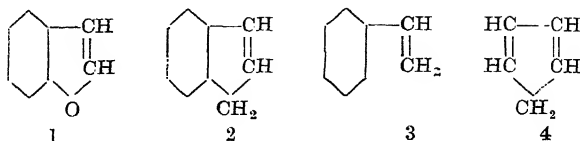
All four types of resin have this in common, that they are produced from cheap materials, some of which are, moreover, available in almost limitless quantity. This is not absolutely the case with regard to phenol-aldehyde resins, as acid tars (phenols) are not available in sufficient quantity for the quantity of resin produced with them to be increased indefinitely, although in case of need the production could be expanded by the production of low temperature tar. The raw materials for cumarone tar are available in ample amount, namely, at least 50,000 to 60,000 tons annually. Aldehyde resins are transformation products of acetaldehyde, which can be produced in unlimited amount from carbide; urea can be produced in indefinitely large quantities as a product of the synthetic nitrogen industry, and there are no limits to the possible production of formaldehyde since the development of the synthesis of methanol from water-gas.

In these directions the classes of resin just named have advantages over any possible competitors, which could with difficulty be met. With regard to products which enjoy similar advantages with regard to raw materials, such as phenol-sulphur resins, the quality of the products is the deciding factor.

**Cumarone Resins.** The production of cumarone resins is the largest manufacturing example of a resin-forming polymerization. The raw material used is the mixture of polymerizable substances contained in Solvent Naphtha (II). According to the investigations of Kraemer and Spilker,<sup>1</sup> these are primarily Cumarone (1), Indene (2), also Styrol (3) and its homologues, and Cyclopentadiene (4). The power of polymerization of these substances has already been discussed (pages 87 *et seq.*: 115

<sup>1</sup> *Ber.*, 23, 78, 84 3169 3269 (1890); 29, 552 (1896); 33, 2257 (1900); 34, 1887 (1901); 36, 645 (1903).

*et seq.*), and therefore the technical development of the process alone be discussed here.



The foundation of the process is the observation that cumarone and indene are polymerized by concentrated sulphuric acid with formation of resinous products. The application of this discovery to the above-mentioned fraction of crude benzole led to the technical cumarone resins. The properties of these products vary extremely with the character of the raw material and of the method of manufacture. Thus, at the present time, almost 40 qualities of cumarone resin are sold, varying from super-pale and elastic qualities to dark-coloured to black "residues" of liquid consistency.<sup>1</sup> The reason for this variety is, that as already indicated, the cumarone resins are fundamentally by-products which accumulate during the necessary purification of the heavy benzole fractions. Their character, therefore, depends to a very great degree on the care with which the distillation processes and the polymerization of the "impurities" are conducted. A special difficulty arises from the fact that the production of the pale, hard products is only possible by using exceptional care in special apparatus, whilst the price obtainable for cumarone resins, at least in Germany, usually renders such precautions unprofitable.

**Manufacture of Cumarone Resins.** The desired result is the production of a pale, hard resin, fast to light and to air. The many proposals which have been made for this purpose will now be discussed in connection with the various stages of the actual manufacturing process.

The general outline of the process of manufacture is as follows. The raw material, the composition of which greatly affects the quality of the product, is a coal-tar fraction of the character of Solvent Naphtha (II), which is first freed from acid

<sup>1</sup> German "War Commission for Fats and Oils" (1916); *Kunstst.*, 9, 190 (1919).

and basic constituents and otherwise pre-treated and dried. The actual polymerization then follows, usually by intimate admixture with small quantities of concentrated sulphuric acid. On standing, the acid, which contains resin in solution, settles to the bottom and is removed. Any remaining acid is then neutralized, the solution washed, and the constituents which have not reacted, containing the cumarone resin in solution, are distilled, leaving the resin as a residue in the still. The quality of the resin therefore depends on—

1. Quality of the solvent naphtha fraction.
2. Purification or pre-treatment of the raw material.
3. Method of polymerization.
4. Separation of the acid resin.
5. Neutralization and washing of the naphtha after polymerization.
6. The distillation process.
7. Any subsequent treatment of the resin so obtained.

**Quality of the Solvent Naphtha.** On treatment with sulphuric acid of the crude solvent naphtha products, previously freed from bases (pyridines, quinolines) and phenols, as was formerly always done in order to obtain benzoles which would not discolour or form resin on standing, a brownish black, semi-liquid mass is obtained, for which scarcely any technical use can be found other than the manufacture of fire-lighters. Valuable resins can only be obtained by treating individual fractions. The following summary of the resins obtainable from

FRACTION	RESIN	
	Percentage of Residue	Character
Up to 160° C. . .	4.9	Viscous liquid <sup>1</sup>
160–180° C. . .	20.3	Hard
180–200° C. . .	35.0	Elastic and hard
200–220° C. . .	12.7	Soft
220–240° C. . .	4.2	Very viscous; semi-solid
240–260° C. . .	6.4	Non-resinous oil

<sup>1</sup> On the use of such a product as a lubricant, see German Pat. 363,291; C. (1923) II, 280.

various coal-tar fractions,<sup>1</sup> previously freed from bases and phenols, is due to E. Glaser.<sup>2</sup>

Apart from homologues of benzene, which predominate, the above fractions contain the following polymerizable substances—

Fraction under 160° C	Styrols and cyclopentadiene
168–175° C	Cumarone (b.p. 172° C.)
176–182° C. <sup>3</sup>	Indene (b.p. 182° C.)
185–200° C. <sup>4</sup>	Methylcumarones
200–210° C. <sup>5</sup>	Methyl indenenes
215–225° C. <sup>6</sup>	Dimethylcumarones

Of these substances cyclopentadiene forms insoluble, black resins on treatment with strong sulphuric acid, and styrol viscous oils of high boiling point. The homologues of cumarone and indene cause the production of soft products when polymerized together with cumarone or indene. The individual substances may, of course, respond to varying degrees to the action of a polymerizing agent, with the formation of products of varying molecular weight; this fact causes many difficulties in technical practice.

The use of the fraction boiling at 150–200° C. has also been proposed for the manufacture of cumarone resins;<sup>7</sup> but in order to obtain valuable products the raw material must be limited to the fraction of boiling point 160–180° C., which is characterized by the presence of cumarone and indene, as recommended by Wendriner,<sup>8</sup> Rabinovitz,<sup>9</sup> and others. The indene, which is contained in this fraction, is characterized by exceptional activity, leading to a very high degree of polymerization. It is, however, easily sulphonated by the sulphuric acid employed as a catalyst. Moreover, indene and indene

<sup>1</sup> On the suitability of low temperature tar for the production of cumarone resin, see Gluud, Breuer, *Ges. Abhandl. zur Kenntnis d. Kohle*, 3, 238 (1918); *C* (1919), IV, 1071.

<sup>2</sup> *Montan. Rundschau*, 11, 635, 668, 704, 736, 776 (1919); *C* (1922), IV, 81.

<sup>3</sup> Kraemer Spilker *Ber.*, 24, 3276 (1891).

<sup>4</sup> Stoermer, *Ber.*, 30, 1700 (1897).

<sup>5</sup> Boes, *Ber.*, 35, 1762 (1902).

<sup>6</sup> Stoermer, Boes, *Ber.*, 33, 3013 (1900).

<sup>7</sup> E. Glaser, *Brennstoffchemie*, 2, 115 (1921). On resin production from the fraction 190–240° C. see British Pat. 156,688 (1921); *Chem. Met. Eng.*, 24, 984 (1921); with strong sulphuric acid.

<sup>8</sup> German Pat. 270,993 (1912).

<sup>9</sup> U.S. Pat. 1,416,062 (1922).

resin have an especial tendency to autoxidation<sup>1</sup> and to consequent discolouration. For these reasons it has been proposed that cumarone and indene should be separated by fractionation and converted into resins separately, in which way a resin of the highest quality would be obtained from the cumarone.<sup>2</sup> The process would, however, presumably be unprofitable in view of the low prices obtainable for cumarone resin of even the highest quality, which are, in turn, due to the overwhelming competition of colophony. The normal raw material for the production of products of high quality is, therefore, that fraction of solvent naphtha which boils at 160–180° C., possibly including fractions boiling up to 185° C., it being of importance for the quality of the resin that the fractionation shall be carried out as carefully as possible.<sup>3</sup>

A variation is introduced by the use of raw materials containing phenols, as in that case the products are soluble in alcohol.<sup>4</sup>

**Purification or Pre-treatment of the Raw Material.** The solvent naphtha fractions are first freed from acid and basic constituents<sup>5</sup> (phenols and pyridines) in the usual manner. The presence of these would deteriorate the resin and involve the use of an increased quantity of sulphuric acid for polymerization. After washing with water the material must be dried, in order that the sulphuric acid subsequently used as a catalyst shall not be diluted or otherwise changed to an uncontrollable degree. Sulphuric acid is used for drying, the proportion and strength of which must be so chosen, with due regard to the quantity of water remaining, that on mixing an acid is obtained which is not too strong and will therefore exercise no polymerizing effect. As a general rule, about 3 to 5 litres of sulphuric acid of 60° Be are required per metric ton

<sup>1</sup> Weger, Billmann, *Ber.*, 36, 640 (1903); Ciamician, Silber, *Ber.*, 46, 417 (1913).

<sup>2</sup> Koch, *Farbe und Lack* (1925), 579.

<sup>3</sup> Regarding technical variations, see Deutsch-Luxemburgische Bergwerks- und Hütten A.-G., S. Hilpert, German Pat. 341,693, 389,232.

<sup>4</sup> Rütgerswerke Akt.-Ges., German Pat. 302,543 (1917); *C.* (1920), II, 131; *Kunstst.*, 9, 318 (1919).

<sup>5</sup> For example, with 4% of sulphuric acid of 50° Bé; Darrin, U.S. Pats. 1,297,328 (1919); 1,326,579 (1919).

of solvent naphtha.<sup>1</sup> Lead-lined or earthenware vessels are used for the operation, as iron is strongly attacked.

As the fractional distillation of solvent naphtha and separation of fractions especially suitable for cumarone resin manufacture is accompanied by certain inconveniences, a pre-treatment has been found advantageous, which is based on the fact that the substances leading to the formation of the dark resins are more easily polymerized than cumarone and indene. Thus, for example,<sup>2</sup> a solvent naphtha fraction, or mixture of fractions, boiling at 135–230° C., is pre-polymerized with an insufficient quantity of sulphuric acid (0.1 to 0.5 per cent of 60–66° Be). On subsequent distillation the substances which form the inferior qualities of resin remain behind in the resinified condition, so that a regular fractionation of the remainder is facilitated and the actual cumarone-indene distillates yield exceptionally pale and hard resins. It is advantageous so to blend the various qualities of solvent naphtha for this purpose that the yield of cumarone resin is about 30 per cent.

In a similar manner a solvent naphtha of boiling point 140–200° C. can be freed from cyclopentadiene and styrol by pre-polymerization with a deficiency of sulphuric acid. On subsequent distillation a dark resin is left, whilst the distillate yields pale products, even when aluminium chloride is used as a catalyst.<sup>3</sup>

The products so obtained are of a pale amber yellow colour, odourless, free from phenols and from the salts of organic sulphonic acids, and evolve practically no sulphur dioxide on dry distillation. The acid value of the resins is 0.25–0.40; the saponification value, 4.0–6.0; iodine value, 5.0–25 per cent; ash contents, 0.05–0.5 per cent; melting point, 90–100° C. The resins yield films which do not become clouded on contact with water.

<sup>1</sup> Miller, U.S. Pat. 1,360,665 (1920); *C.* (1921), II, 267; *Kunstst.*, 12, 31 (1922).

<sup>2</sup> The Barrett Company, German Pat. 400,030 (1920); *Kunstst.*, 15, 11 (1925); *C.* (1924), II, 2429; British Pat. 142,806; *C.* (1922), IV, 466; *Kunstst.*, 11, 6 (1921); French Pat. 514,759; *Kunstst.*, 12, 70 (1922).

<sup>3</sup> The Koppers Company (assigned by H. C. Karns), U.S. Pat. 1,541,226 (1917); *C.* (1925), II, 2103; *Kunstst.*, 16, 75 (1926); British Pat. 132,229; *Kunstst.*, 10, 79 (1920).

**The Polymerizing Process.** The solvent naphtha fraction, which has been purified and dried as indicated above, is then subjected to the action of polymerizing agents, among which sulphuric acid of a definite strength is preferred. Sulphuric acid of 66° Be is ordinarily used in the proportion of 3 to 5 per cent, on the assumption that the solvent naphtha fraction contains 30 to 40 per cent of polymerizable constituents.<sup>1</sup> If pale resins are to be produced, the reaction, which is strongly exothermic, must be moderated by cooling and by gradual addition of the acid, so that the temperature may not rise above 20° C.<sup>2</sup> For the production of resins of the best quality, the upper permissible temperature limit and the quantity or concentration of the sulphuric acid are inter-related. Thus, M. Wendriner<sup>3</sup> recommended the use of 0.25–0.40 volumes per cent of sulphuric acid of 66° Be at a reaction temperature of 40–50° C. If weaker sulphuric acid is used softer resins are obtained, which are also darker on account of the higher reaction temperature which is then necessary. Thus, in an older patent specification,<sup>4</sup> Wendriner described the use of 3 to 5 volumes per cent of sulphuric acid of 60° Be which are mixed with the solvent naphtha, after which 0.25 volumes per cent of sulphuric acid of 66° Be are gradually added, whilst the materials are intimately mixed and gradually raised to a temperature of 110–120° C. When using acid of 46–48° Be a viscous oil is obtained as the polymerized product, after separating the acid (which can be recovered without loss) and after distilling off the portions which have not entered into reaction; this oily polymerizate can only be used after distillation, by which it is separated into an oil and a resin suitable for varnish production.<sup>5</sup> But the use of sulphuric acid of concentration greater than 66° Be, or in larger proportions of that strength

<sup>1</sup> Miller, U.S. Pat. 1,360,665 (1920).

<sup>2</sup> Barrett Co., German Pat. 420,465 (1920); *C.* (1926), I, 1300; *Kunstst.*, 16, 76 (1926); P. Miller, U.S. Pat. 1,360,665 (1920); *Kunstst.*, 12, 31 (1922); *C.* (1921), II, 267; P. Miller, Barrett Co., British Pat. 160,148 (1920); *C.* (1921), IV, 132; *Kunstst.*, 12, 46 (1922).

<sup>3</sup> German Pat. 281,432 (1913); *Kunstst.*, 5, 33, 279 (1915); *C.* (1915), I, 232.

<sup>4</sup> German Pat. 270,993 (1912); *C.* (1914), I, 1131; *Kunstst.*, 5, 278 (1915).

<sup>5</sup> Demant, British Pat. 179,610 (1921).



than are described above, is undesirable.<sup>1</sup> Apart from increased formation of insoluble acid resins, the production of strongly emulsifying sulphonic acids has a very harmful effect, as these make the separation of the acid resins difficult, and it is mainly these acid resins which cause the dark colour of cumarone resin. Moreover the formation of sulphonic acids causes losses in the yield, and deteriorates in other ways the quality of the products.<sup>2</sup>

The necessity of intimately mixing the solvent naphtha with the very much heavier and insoluble sulphuric acid, and the desire to keep the mixture cool, in order to neutralize the effect of the very large quantities of heat which are liberated, have led to the development of special apparatus and methods of operation.<sup>3</sup> It has been found advantageous for the production of pale and hard resins, to leave the naphtha containing the polymerizable constituents in contact with the acid for as short a time as possible; this necessitates the use of fairly vigorous polymerizing agents and rapid cooling contrivances of large capacity.

C. Ellis<sup>4</sup> describes a suitable form of apparatus, consisting mainly of a receiver provided with a pump. The pump continuously withdraws the solvent naphtha from the floor of the receiver and conveys it to the top, by which means thorough mixing is attained. The receiver may, advantageously, be provided with cooling tubes through which cold water or cold brine from a refrigerating plant is circulated.

E. Glaser<sup>5</sup> describes the required plant as follows, but it should be noted that he is considering the washing of benzole in quite a general fashion, and is not, therefore, considering the special requirements involved in the recovery of cumarone resin.

<sup>1</sup> For example, German Pat. 53,792 of the A.G. für Teer- und Erdölindustrie recommends 10% of concentrated sulphuric acid.

<sup>2</sup> Thus such resins may form films which are washed away by water. By treatment with 1 to 2% of sulphur at 150° C. the power of forming emulsions with water is often destroyed, but this appears to deteriorate the colour of the resin.

<sup>3</sup> See the Barrett Co. U.S. Pat. 1,464,851; *C.* (1923), IV, 803; U.S. Pat. 1,515,315 (1921); *C.* (1925), I, 1137; Plants for continuous working; see British Pat. 246,491.

<sup>4</sup> *Synthetic Resins and Their Plastics*, pp. 58 *et seq.*

<sup>5</sup> *Montan. Rundschau*, 11, 638 (1919)

The benzole washers now used are always cylindrical, vertical tanks, provided with stirring gear, and with hemispherical or, preferably, conical bottoms, in order to facilitate the removal of the acid used for purification. The stirrer usually takes the form of a four-bladed propeller which may turn about either a horizontal or a vertical axis. Both arrangements have advantages and disadvantages. With a horizontal shaft the stirrer bales up the acid at the bottom, and therefore requires relatively little driving power, but the mixing with the deep layer of oil above is a slow process. Moreover, this arrangement necessitates at least one stuffing-box which comes into contact with the acid and therefore requires exceptional care to maintain it tight. No stuffing-box is required with stirrers on a vertical shaft, but the power requirements are greater, as the acid is only thoroughly mixed with the oil at a rapid rate of revolution. Those parts of the washer and stirrer which come into contact with the charge are coated with lead, preferably homogenously. Among mechanical appliances for benzole washing we may mention Sexauer's intensive stirrer, and<sup>1</sup> a type known as the "Rapid Mixer."<sup>2</sup> The benzole washers usually have a capacity of 3,000 to 10,000 litres and are ordinarily surrounded by an operating platform from which the supply of benzole and of acid can be regulated. The acid is measured in a measuring tank placed above the washer, from which it is generally added in more than one portion.

The progress of the polymerization can be followed by determinations of the specific gravity, which rises as the oil is polymerized. If two samples, taken before and after an addition of acid, show the same specific gravity, the polymerization is completed.

Other polymerizing agents than sulphuric acid have been proposed, more particularly anhydrous reactive chlorides,<sup>3</sup> such as aluminium chloride,<sup>4</sup> ferric chloride,<sup>5</sup> and others, also phosphoric acid.<sup>6</sup> According to Marcusson,<sup>7</sup> cumarone resins of exceptionally high melting point, up to 160° C., are obtained with metallic salts, whilst those obtained with sulphuric acid have a melting point which never exceeds 65° C. Further investigations on polymerizing agents were carried out by

<sup>1</sup> Lunge and Köhler, *Steinkohlenteer und Ammoniak* (1912) I p. 868.

<sup>2</sup> *Idem.* p. 686.

<sup>3</sup> Demant, German Pat. 392,090 (1917); *C.* (1924), II, 2429; *Kunstst.*, 15, 11 (1925).

<sup>4</sup> Heussler, *Angew.*, 9, 319 (1896).

<sup>5</sup> Crystallized, that is, hydrated ferric chloride is recommended by Oberschlesische Kokswerke A.-G. and A. Supan, German Pat. 394,217 (1923); *C.* (1924), II, 2429; *Kunstst.*, 15, 11 (1925); see also German Pat. 446,707.

<sup>6</sup> British Pat. 179,610 (1921).

<sup>7</sup> *Chem.-Ztg.*, 43, 93 (1919); I. G. Farbenind. A.-G., German Pat. 446,707 (1918).

C. Ellis,<sup>1</sup> who found that silver oxide was very active, whilst zinc chloride<sup>2</sup> and anhydrous tin chlorides were less active.<sup>3</sup> Iodine, phosphorus trichloride, chromic acid, hydrochloric acid, ammonium dichromate, formaldehyde and potassium hydroxide were without effect.

According to other processes polymerization is effected by heating under pressure, with or without catalysts, such as copper, silver, gold, or platinum.<sup>4</sup> The velocity of polymerization may be controlled by dilution of the solvent naphtha with lighter fractions of boiling point 130–150° C.<sup>5</sup>

**Separation of the Acid Resin.** After polymerization is completed the batch is allowed to stand for a short time, during which a mixture of acid resin insoluble in solvent naphtha and of acid separates, which must be carefully removed, as otherwise any acid resin which became mixed with the cumarone resin would result in black coloration and poor solubility. The acid resin obtained with sulphuric acid of 66° Be is viscous, and its separation from the oil is attended with more or less difficulty. It usually amounts to 1 to 2 per cent of the solvent naphtha used.<sup>6</sup>

**Neutralizing and Washing the Solvent Naphtha after the Polymerization.** After the removal of the acid resin, the solvent naphtha which contains the cumarone resin in solution undergoes several washing and neutralizing operations, the sequence and number of which may vary, and which must be completed by thorough washing with water. If this washing is incomplete salts are left in the resin, which attack the still during the subsequent distillation and deteriorate the quality of the resin considerably. (See page 241 *et seq.*)

<sup>1</sup> *J. Ind. Eng. Chem.*, 8, 797 (1916); *Chem. News*, 116, 104 (1917); Ellis and Rabinovitz, *Angew.*, 32, 72 (1919).

<sup>2</sup> Stoermer, *Ann.*, 312, 244, 264 (1900).

<sup>3</sup> E. Stern, *Angew.*, 32, 247 (1919).

<sup>4</sup> Sperr, Darrin, U.S. Pats. 1,263,813 (1918); 1,296,776 (1919); Canadian Pat. 184,890 (1918); British Pat. 123,806 (1918); see also U.S. Pat. 1,314,613 (1919); H. Coppers Co., French Pat. 491,997; *Kunstst.*, 10, 198 (1920).

<sup>5</sup> Capthorne, Tannehill, U.S. Pat. 1,353,220 (1920); *J. Ind. Eng. Chem.*, 8, 797 (1916).

<sup>6</sup> C. Ellis, *Synthetic Resins and Their Plastics*, p. 60; the acid resin is separated from the sulphuric acid by addition of water; on the recovery of the waste acid, see Lunge and Köhler, *Steinkohlenteer und Ammoniak*, Fifth Edition, Vol. I, pp. 874 *et seq.* See also E. Glaser, *Seife* (1919), No. 9–10.

Neutralization may be effected, for example, by caustic soda solution of specific gravity 1.2 or 1.3, or by a solution of sodium carbonate or other substances. Capthorne<sup>1</sup> proposes the interruption of the polymerization at any desired stage, by the addition of ammonia. On neutralizing and washing with dilute alkali solutions or water, stable emulsions are often formed which render the completion of the desired operations difficult or impossible. As even traces of remaining acids or salts cause discoloration during the subsequent distillation and have other bad effects on the quality of the resin, various proposals have been made for avoiding the formation of such emulsions. F. H. Meyer<sup>2</sup> neutralizes by mixing anhydrous, very finely-powdered carbonates of the alkali or alkaline earth metals, to which a small amount of sodium or barium peroxide may advantageously be added, to the acid resin solution with vigorous stirring. After 12 to 24 hours the salts have separated completely, after which the clear resin solution may be further treated. Salt solutions are then recommended for washing, in order to avoid the formation of emulsions<sup>3</sup> and also washing with hydrochloric acid,<sup>4</sup> and finally warming to 70-80° C. Clark M. Dennis<sup>5</sup> recommends dilution with purified solvent naphtha before washing. It is alleged that the formation of emulsions can be avoided with more certainty than by the methods just referred to, by the use of electrical or centrifugal separation, by the addition of certain colloids and by the use of other processes which impede emulsification.<sup>6</sup>

**The Distillation Process.** After neutralizing and washing.

<sup>1</sup> E. Glaser, *Brennstoffchem.*, 2, 115 (1921).

<sup>2</sup> German Pat. 294,107 (1916); *Kunstst.*, 6, 263 (1916); C. (1916), II, 707; Walpole, British Pat. 145,415 (1920); *Kunstst.*, 11, 15 (1921).

<sup>3</sup> Wade, British Pat. 166,818 (1920); The Barrett Co., French Pats. 520,850, 521,678 (1920); C. (1921), IV, 872, 2069; German Pat. 352,520; P. Miller, U.S. Pat. 1,395,968 (1921); 20% sodium chloride solution, C. (1923), IV, 729; *Kunstst.*, 13, 125 (1923); Roberts and Rhodes, U.S. Pat. 1,413,558 (1922).

<sup>4</sup> Barrett Co., Miller, British Pat. 149,982 (1920); C. (1921), II, 75; *Kunstst.*, 11, 15 (1921); Miller and Rhodes, British Pat. 160,148 (1920); U.S. Pat. 1,365,423 (1921); C. (1921), II, 75 (267,563); Canadian Pat. 217,332 (1922); French Pat. 514,759 (1922); *Kunstst.*, 12, 70 (1922); Miller, U.S. Pat. 1,360,665 (1920); see also French Pat. 524,238.

<sup>5</sup> The Barrett Co., U.S. Pat. 1,468,440 (1919); C. (1924), I, 251.

<sup>6</sup> *Farbe und Lack* (1925), 505; Furness, *J. Soc. Chem. Ind.*, 33, 1000 (1923).

the non-polymerized constituents of the solvent naphtha, which hold the resin in solution, are distilled. The distillation may be more effectively conducted by the aid of direct steam, or reduced pressure, or both.<sup>1</sup> After the solvent naphtha, naphthalene distils over, and the water in the coolers must then be kept warm; finally, a heavy oil is driven over, which is probably a polymer of indene, and which boils at 320–330° C. at the ordinary pressure. Distillation is continued until a sample of the residual resin shows a sufficiently high melting point.

As has been re-established by G. Schneider,<sup>2</sup> if pale, hard and elastic resins are to be obtained the temperature must be kept low, not only during polymerization, but also during distillation of the solvent naphtha. According to a communication by C. Ellis, the experience of varnish makers shows that cumarone resins cannot be exposed to temperatures above 275° C. without becoming dark in colour.

Before the distillation of the solvent naphtha additions may already be made, for example, of natural resins, drying oils, waxes, and so forth, in order to render the final product more suitable for the production of varnishes, varnish oils, and the like.<sup>3</sup>

**After-treatment of the Resin.** Various proposals have been made for improving the properties of cumarone resins. Thus, Singer<sup>4</sup> purifies crude cumarone resins by treatment with alcohol acetone or chlorinated hydrocarbons. C. Knüppel<sup>5</sup> treats the polymerization products of cumarone and indene with a powerful current of air at a comparatively high temperature for three to six hours, whilst in a state of fine division, thus obtaining a harder product. Lender<sup>6</sup> heats with sulphur

<sup>1</sup> Rabinovitz, U.S. Pat. 1,416,062 (1922); *C.* (1922), IV, 590; *Kunstst.*, 14, 42 (1924); Canadian Pat. 203,100 (1920).

<sup>2</sup> *Ber. der Ges. für Kohlentechnik* (1921), 39; *C.* (1922), II, 329; see also Wendriner, German Pat. 281,432 (1913); *Kunstst.*, 5, 279 (1915).

<sup>3</sup> Chem. Fabr. Worms A.-G., German Pat. 348,088 (1909); *C.* (1922), II, 704; Lender, Koch, German Pat. 245,634 (1911); U.S. Pat. 1,019,666 (1912).

<sup>4</sup> Norwegian Pat. 29,034 (1918).

<sup>5</sup> German Pat. 253,437 (1912); *Kunstst.*, 3, 88 (1913); 5, 279 (1915); see also Schwarz, German Pat. 322,802 (1918); *C.* (1920), IV, 410; *Kunstst.*, 10, 204–5 (1920).

<sup>6</sup> German Pat. 277,605 (1913); *C.* (1914), II, 742; *Kunstst.*, 4, 335 (1914); Dutch Pat. 138 (1914); *Angew.*, 27, 11 (1914); see also Schlatter, U.S. Pat. 1,294,838 (1919).

or sulphur chloride under pressure. According to another process the sulphur of cumarone resin is reduced, and the hardness increased, by treatment with concentrated sulphuric acid in the presence of solvents.<sup>1</sup> Crude cumarone resins, which contain the sulphonic acids of aromatic hydrocarbons, may be hardened by melting with basic compounds, such as NaOH, Ca(OH)<sub>2</sub>, MgO, ZnO, and so forth.<sup>2</sup> It is not known to what extent processes of this nature are used in practice. Any sensitiveness to water, caused by the presence of sulphonic acids, can be removed by heating with 1 to 2 per cent of sulphur.

### PROPERTIES OF CUMARONE RESINS

Cumarone resins represent mixtures of various highly polymerized substances, which vary fairly considerably in character, according to the composition of the raw material and the degree of care used in production, more especially in the distillation. The varying properties of commercial cumarone resins are due to the dependence of the polymerizing process on many factors. The better qualities consist almost exclusively of polymers of cumarone and indene, whilst the poorer qualities also contain polymers of their homologues and of cyclopentadiene, styrol, and other products. Marcusson<sup>3</sup> was able to establish certain relations between the composition and properties of these resins. Thus the colour depended on the proportion of constituents insoluble in acetone (acid resin). It was also found that the melting point of the resins was highest when they contained the least quantities of constituents soluble in ether-alcohol, which are presumably low melting polymers of indene and styrol condensation products with benzene homologues, or high boiling tar oils. On the other hand, the melting point rises with increase of the constituents insoluble in ether-alcohol, such as paracumarone and paraindene, of high melting

<sup>1</sup> Rütgerswerke, German Pat. 325,575 (1918); *C.* (1920), IV, 606; see also Marcusson, *Chem.-Ztg.*, 43, 109 (1919).

<sup>2</sup> Ellis-Foster Co. (assigned by C. Ellis), U.S. Pat. 1,570,584 (1917); *C.* (1926), I, 2852.

<sup>3</sup> *Chem.-Ztg.*, 43, 93, 109, 122; *C.* (1919), IV, 14; *Mitteil. aus dem Materialprüfungs-Amt.*, 38, 69; *C.* (1921), IV, 1230.

point. The behaviour of the various qualities of resin is summarized in the following table—

SEPARATION OF CUMARONE RESINS BY SUCCESSIVE  
TREATMENT WITH ALCOHOL-ETHER AND ACETONE  
ACCORDING TO MARCUSSEN (*loc. cit.*)

Quality No.	External Characters	Behaviour with Alcohol-Ether		Insoluble in Acetone	
		Soluble %	Insoluble %	Organic %	Inorganic %
1	Very Hard—Pale	47	53	0	0
2	Pale brown	48	52	0	0
5	Black	64	17	8.3	7
6	Hard—Pale	56	44	0	0
7	Pale brown	58	42	0	0
11	Medium Hard—Pale	67	32	0	0
15	Black	55	34	11	0
16	Soft—Pale	69	30	0	0
20	Black	69	15.5	12.5	0
23	Viscous—Brown	84	1.0	2	5
28	Liquid—Brown	73	7.3	2	0
30	Black	76	4.7	4.4	3

The commercially available cumarone resins show colours which vary from very pale yellow, through yellow, brown, and dark brown to black. They represent very hard, hard or soft to liquid products, the melting points of which fall in accordance with these characteristics. The commercial qualities have been classified according to hardness and colour into 34 different classes.<sup>1</sup> On the basis of the softening point, determined by the Kraemer-Sarnow method, the following degree of hardness are distinguished—

Very Hard	Softening point over 50° C.
Hard	“ “ 40–50° C.
Medium Hard	“ “ 30–40° C.

The nail test distinguishes further between soft, viscous, and

<sup>1</sup> Report on the work of the Sub-Committee on the Classification of “Cumarone Resins,” *Kunstst.*, 9, 190 (1919); *C.* (1920), II, 450; see also pp. 254 *et seq.*

liquid resins. Standards have also been established with regard to colour, and pale, pale brown, brown, dark and black products are distinguished.<sup>1</sup> (See also page 255.) Although at the time of their introduction such a classification seemed indispensable in view of the very large output, some of these classes are scarcely used to-day. A different classification has been adopted in the United States,<sup>2</sup> where 5 classes are distinguished according to the melting point and intended application.

Rubber Grade S	Melting point	50-65° C.
Medium Soft .	..	65-85° C.
Rubber Grade H	..	85-100° C.
Medium Hard .	..	100-135° C.
Varnish Grade	..	135-150° C.

In this case the description of the colour is analogous to that used for colophony (rosins), and cumarone resin No. 1 corresponds to colophony N, whilst cumarone resin No. 3 corresponds in colour to colophony G.<sup>3</sup> These resins increase in value with hardness and paleness.

Solid cumarone resins have a specific gravity of about 1.2 to 1.3, show a conchoidal fracture, and have an odour somewhat resembling gum benzoin. H. Wolff found acid ratios of between 1 and 20, saponification values of 1 to 25, and iodine values of 23 to 39.

Cumarone resins dissolve easily<sup>4</sup> in benzene and its homologues, solvent naphtha, and so forth. They are also soluble in turpentine oil, acetone, ether, ethyl acetate, amyl acetate, and so forth, and also in carbon tetrachloride, chloroform, trichlorethylene and carbon disulphide. They are not completely soluble in most light petroleum spirits, but become soluble after the addition of benzene, and so forth. Cumarone resins

<sup>1</sup> On a further commercially recognized method of classifying the very hard and super-pale resins, see p. 322 ; R. Fischer, *Farbenztg.*, 26, 2275 (1921), discusses the price fluctuations of various classes from 5th Oct., 1916, to May, 1921.

<sup>2</sup> See C. Ellis, *Synthetic Resins and Their Plastics*, p. 40.

<sup>3</sup> According to the colour standards of E. Fonrobert and F. Pallauf, American Resin N corresponds to Fonrobert No. 29 and Resin G to Fonrobert No. 136.

<sup>4</sup> Bottler, *Kunstst.*, 5, 277 (1915).



are only slightly soluble in alcohol.<sup>1</sup> They are completely miscible with rosin oil, pine oil, stearic acid, ozokerite, gilsonite, japan wax, carnauba wax, beeswax, and so forth; on the contrary, paraffin oil, ceresine, and paraffin wax dissolve limited quantities only.<sup>2</sup>

The viscosity of solutions of cumarone resins is greater than that of corresponding solutions of colophony and its esters.

The chemical character of cumarone resins, which are essentially mixtures of cumarone and indene polymers, is manifested partly by a certain susceptibility to oxidation, due to indene derivatives, but more particularly by stability to saponifying agents. Thus, cumarone resins are usually unaffected by the action of 5 per cent sodium carbonate solution, 1 and 5 per cent caustic soda solutions, and 10 per cent ammonia solution; on warming with 5 per cent caustic soda solution a slight effect is observable,<sup>3</sup> which is probably due to the presence of impurities. C. Ellis studied the effect of a paste of Portland cement and water.<sup>4</sup> Films of cumarone resin proved to be exceptionally resistant compared with those from drying oils and natural resins.

Cumarone resins are decomposed on heating to 300–400° C. with reversal of the polymerization process, the main product being cumarone or very considerably depolymerized paracumarone, together with indene, hydrindene and small amounts of phenol.

The oil so obtained, which E. Stern<sup>5</sup> named "Cumarone oil," can be reconverted into solid resins or other oils, a reaction which was specially studied by Stern, more especially with regard to the activity of various catalysts. Cumarone oil behaves otherwise as a non-drying oil, although if oxygen carriers such as lead or manganese resinate are added, it

<sup>1</sup> On Cumarone resins soluble in alcohol, see German Pat. 302,543 of Rütgerswerke A.G.

<sup>2</sup> C. Ellis, *Synthetic Resins*, p. 42.

<sup>3</sup> Bottler, *Kunstst.*, 5, 278 (1915); J. Marcusson, *Chem-Ztg.*, 43, 93 (1919).

<sup>4</sup> U.S. Pats. 999,439 (1911); 999,708, 1,005,818, 1,006,737 (1911); Ellis and Wells, 1,179,413; Ellis, 1,189,549, 1,189,551 (1916); 1,246,827 (1917); British Pat. 117,016 (1917); C. Ellis, L. Rabinovitz, *J. Ind. Eng. Chem.*, 8, 797 (1916); *Kunstst.*, 9, 192 (1919).

<sup>5</sup> *Angew.*, 32, 246 (1919); *C.* (1919), IV, 667; *Kunstst.*, 11, 141 (1921).

acquires the properties of a drying oil, constituting a case of a remarkable acceleration of a polymerization process by an oxidation catalyst.<sup>1</sup>

### APPLICATIONS OF CUMARONE RESINS

In Germany, especially during the war, cumarone resins were widely used as the basis of printing inks, varnishes and paints, as a varnish oil substitute and for sizing paper. The utility of these products, the quality of which has been considerably improved, is shown by the fact that they have partly maintained their position since the war, and also that their use has become firmly established in other countries and especially in the United States, which have not suffered from a dearth of raw materials.

**Cumarone Resins for Varnishes.**<sup>2</sup> Spirit varnishes, that is, varnishes which form a hard film merely by the evaporation of the solvent, can easily be prepared from cumarone resins and hydrocarbons, especially solvent naphtha, by the usual methods. According to Krumbhaar<sup>3</sup>, slight changes take place in the film after such varnishes have dried by evaporation of the solvent, due to the slow volatilization of high-boiling constituents of the resin. There is also a further oxidation of the para-indene (causing a yellow colour) and partial polymerization of the paracumarone. In spite of these reactions the film remains soluble, so that a second coat can only be applied with softening or solution of the under coat. The film is only slightly elastic, and shows but little resistance to weathering. There is also a very decided tendency to discoloration. On the other hand, films of cumarone resin offer certain advantages, which are due to the chemical nature of the basic material and are manifested by chemical inertness to pigments, a certain degree of fastness to water and a conditional fastness to acids and alkalis. As the films are greatly improved by very

<sup>1</sup> The same must be assumed in the case of tung oil.

<sup>2</sup> See also H. Rudolf, *Farbe und Lack* (1924), 217.

<sup>3</sup> *Farbenzeitg.*, 21, 1086; *Kunstst.*, 7, 97 (1917); *C.* (1916), II, 777; W. Urbanus, *Kunstst.*, 16, 144, 175, 248 (1926); 17, 7 (1927); *Allg. Öl- und Fett-Ztg.*, 24, 415, 427 (1927).

small additions of drying oil, such films, which are much more elastic, have found numerous special applications.

Kraemer and Spilker<sup>1</sup> already proposed the use of solutions of cumarone resins as varnishes. Benzene, benzene, solvent naphtha, turpentine oil,<sup>2</sup> and mixtures of paraffin and aromatic hydrocarbons have been recommended as solvents.<sup>3</sup> Among others, the following materials have been recommended as additions in order to improve the product: 5 to 10 per cent of animal or vegetable oils, in the form of the calcium salts of their fatty acids,<sup>4</sup> nitrobenzene,<sup>5</sup> rubber,<sup>6</sup> chlorinated rubber,<sup>7</sup> and tung oil.<sup>8</sup> Cumarone resins may also be used jointly with wax<sup>9</sup> or zinc resinate.<sup>10</sup> The use of solutions of cumarone resin has been proposed for the manufacture of waterproofing solutions and coatings.<sup>11</sup> They played an important part during the war as linseed oil and varnish oil substitutes,<sup>12</sup> a part which vanished with the re-establishment of normal conditions.

Their neutral character renders solutions of cumarone resin especially suitable for the production of coloured enamels.<sup>13</sup> The varnishes have also been recommended<sup>14</sup> as vehicles for

<sup>1</sup> *Ber.*, 23, 81 (1890).

<sup>2</sup> Eichler, U.S. Pat. 1,133,432 (1915); *Kunstst.*, 5, 213 (1915); see also U.S. Pat. 1,133,433.

<sup>3</sup> C. Ellis, U.S. Pat. 1,451,092; *Kunstst.*, 14, 42 (1924).

<sup>4</sup> Sprengler, German Pat. 254,767 (1911).

<sup>5</sup> Dayol, French Pat. 514,405; *Kunstst.*, 12, 70 (1922).

<sup>6</sup> Holzapfel, U.S. Pats. 1,430,083 (1922); 1,481,801 (1922); *Kunstst.*, 13, 57 (1923).

<sup>7</sup> Chadsloid Chemical Co., H. Boehmer, U.S. Pat. 1,572,065 (1923); *C.* 1926), I, 3281.

<sup>8</sup> Kessler, U.S. Pat. 1,411,035 (1922); *C.* (1922), II, 1177.

<sup>9</sup> Robeson, U.S. Pat. 1,405,941 (1922).

<sup>10</sup> J. Wolf, German Pat. 351,816 (1917); *C.* (1922), IV, 167.

<sup>11</sup> See C. Ellis, U.S. Pats. 999,439 (1911); 999,708 (1911); 1,005,818 (1911); 1,381,863 (1922); 1,412,014 (1922); McCoy, U.S. Pat. 1,299,847 (1919); Edison, U.S. Pat. 1,364,359 (1921).

<sup>12</sup> See Deutsch-Luxemburgische Bergwerks- und Hütten-A.-G., S. Hilpert, German Pats. 319,010, 320,808 (1916); *C.* (1920), IV, 45, 225; *Kunstst.*, 10, 68, 190 (1920); jointly with acid resins; Darrin, U.S. Pats. 1,315,658 (1919); 1,382,345 (1921); *C.* (1921), IV, 810. See also Farbenf. vorm. F. Bayer & Co., German Pat. 305,515 (1917), and Stern, German Pat. 345,816 (1919), on the use of benzylindene, cumarone, or indene as linseed oil substitute.

<sup>13</sup> Blass, U.S. Pat. 1,401,034 (1921).

<sup>14</sup> Fehringer, German Pat. 331,152 (1914); *C.* (1921), II, 563; *Kunstst.*, 11, 22 (1921); U.S. Pat. 1,157,768 (1915); *Kunstst.*, 9, 124 (1919); Shilvock, U.S. Pat. 1,411,673 (1922); addition of small amounts of stearic acid.

bronze powder, as the coatings are sometimes exposed to very slight wear only. Quick drying paints for ships' bottoms are frequently prepared from cumarone resin spirit varnishes to which small quantities of drying oil have been added.<sup>1</sup>

In other respects such cumarone resin spirit varnishes are of but little importance. It is possible that there is a future for the use of cumarone resins in conjunction with pitches, and so forth,<sup>2</sup> and also in conjunction with cellulose esters.<sup>3</sup>

The real importance of cumarone resins consists, however, in their use as components of oil varnishes, in the production of which they are already used in considerable amount. They are soluble in tung oil, linseed oil, perilla oil, and other drying and non-drying oils. It has, however, been found that in order to incorporate them satisfactorily with fatty oils it is necessary to heat for quarter to half an hour to a temperature of at least 260° C., but not exceeding 300° C., in case varnishes of high quality are required. If the heating is insufficient the resin shows a tendency to separate. If the maximum temperature is exceeded a strong discoloration results. When using tung oil, which, as is well known, shows a tendency to thicken unduly or to gelatinize at temperatures above 200° C.,<sup>4</sup> it must be remembered that cumarone resins do not delay or prevent this reaction in the same manner as, for example, does colophony, in consequence of its great dissolving power.

Such an oil varnish may, for example, be prepared as follows:<sup>5</sup> 30 to 35 parts of pale, very hard cumarone resin are heated in a varnish pot with 15 to 20 parts of prepared linseed

<sup>1</sup> Schwarz, Heiter, *Farbe und Lack* (1924), 346; but regarding suitability see M. Ragg, *Die Schiffsboden- und Rostschutzfarben*, Berlin (1926), p. 72.

<sup>2</sup> The Koppers Co., U.S. Pats. 1,292,907-8 (1919); Canadian Pat. 188,272 (1919); see also Darrin, U.S. Pat. 1,296,776 (1919); British Pat. 129,264 (1919); 118,079 (1917); 132,229 (1919); 138,068 (1919).

<sup>3</sup> F. Lehmann, Stocker, German Pat. 281,373 (1912); U.S. Pat. 1,185,514 (1916); Austrian Pat. 72,978; *Kunstst.*, 7, 249 (1917); French Pat. 471,104; *Kunstst.*, 12, 23 (1922); German Pat. 297,149 (1913); *Kunstst.*, 7, 115 (1917); U.S. Pat. 1,191,801; *Kunstst.*, 7, 9 (1917); Austrian Pat. 71,287 (1915); *Kunstst.*, 7, 12 (1917); French Pat. 469,925; *Kunstst.*, 7, 239 (1917); Zapon-Lack-Ges m. b. H., German Pat. 281,265 (1913); *Kunstst.*, 5, 33 (1915); see also L. Lilienfeld, U.S. Pat. 1,625,416 (Combination with cellulose ethers, etc.); see also A. Rogers, C. Banta, *Ind. Engin. Chem.*, 20, 198; C. (1928), I, 2014.

<sup>4</sup> E.g. at 285° C. in about 10 minutes.

<sup>5</sup> *Seifensieder Ztg.* (1917), 773.

oil or tung oil, or a mixture of linseed varnish oil and stand oil, to 250–275° C., and maintained at this temperature for half an hour; 1 part of molten lead-manganese resinate and 0.1 part of freshly prepared calcium hydroxide are then added. The mixture is occasionally stirred until these materials have been incorporated, after which the melt is allowed to cool, and thinned, for example with turpentine oil, to the required consistency.

In a similar manner oil varnishes of the most varied character can be produced, both medium oil and short oil, and also varnishes which contain other components in addition. Sometimes a slight turbidity is observed in such varnishes, which can usually be removed by a slight increase in the temperature of boiling or a subsequent addition of a small amount of colophony or turpentine oil. In consequence of the tendency to discoloration at high temperatures, the permissible degree of heating must be found experimentally in each case. The fatty oils must, of course, be so far pre-treated before mixing that by boiling with the cumarone resin the required product is produced.<sup>1</sup>

Oil varnishes prepared from cumarone resins are of about equal utility with those prepared from esterified rosin with the same proportion of oil. This is, however, truer with regard to stability on storage than with regard to fastness to light, which is not as good as might be wished, the varnish showing a tendency to discoloration. The possibility of using such varnishes for admixture with pigments, which is otherwise very attractive on account of the fine lustre of the film, is naturally reduced by this disadvantage, which has not yet been fully overcome.

**Cumarone Resins for Printing Ink Varnish Oils.** According to Marcusson,<sup>2</sup> cumarone resin has partially replaced stand oil

<sup>1</sup> On special processes see Lender, Koch, U.S. Pat. 1,019,666 (1912); German Pat. 245,634 (1911); Lender, French Pat. 434,768; *Kunstst.*, 10, 118 (1920); Eichler, U.S. Pats. 1,133,432–3 (1915); *Kunstst.*, 5, 213 (1915); Darrin, U.S. Pats. 1,315,658 (1919); 1,382,345 (1921); *C.* (1921), IV, 810; U.S. Pat. 1,370,195 (1921); Briggs, British Pat. 168,293 (1921); M. Kessler, U.S. Pat. 1,411,035 (1922); *C.* (1922), II, 1177; see also King, Bayard, Rhodes, *J. Ind. Eng. Chem.*, 12, 549 (1920); *C.* (1920), IV, 343.

<sup>2</sup> *Chem.-Ztg.*, 43, 93 (1919); see also Rübencamp, *Farbenztg.*, 25, 272; *C.* (1920), II, 131.

in the printing ink industry, in the form of qualities 16 to 30, which possess the viscosity required for printing ink manufacture, but are too adhesive and have therefore to be diluted, for which purpose stand oil is used for delicate and valuable work, mineral oil or tar oils for rough newspaper print, and so forth, or for the latter purpose residues containing cumarone resin may also be added. The prints show an improved lustre, and the varnishes are less affected by the pigment. The use of cumarone resin for these purposes is largely a question of price.

**Other Actual or Proposed Applications.** According to C. Ellis,<sup>1</sup> the addition of about 5 per cent of cumarone resin to rubber has a softening effect, which enables the material to be more easily worked.<sup>2</sup> The process offers special advantages, and has been introduced in part in America. A typical American application is for the manufacture of chewing gum,<sup>3</sup> for which purpose very large quantities of cumarone resin have already been used, to the extent of 7 to 10 per cent, in the form of a resin product which has been specially freed from high-boiling impurities, and which must obviously be miscible with the other constituents of the chewing gum.

The good dielectric properties of cumarone resins have led to the use of such resins for press-moulded articles, in which the resins are used either alone or in conjunction with various fillers.<sup>4</sup>

Cumarone resins are also used instead of the usual rosin soaps for sizing paper. As the artificial resins cannot be saponified, they are converted into an emulsion with the help of rosin soap or the alkali salts of aromatic sulphonic acids or naphthenic acids, and then applied in the usual manner.<sup>5</sup>

<sup>1</sup> *Synthetic Resins and Their Plastics*, pp. 47 et seq.

<sup>2</sup> Wells, U.S. Pat. 1,248,226 (1917).

<sup>3</sup> Weber, U.S. Pats. 1,248,961 (1917); 1,402,817 (1922).

<sup>4</sup> Baekeland, U.S. Pat. 1,038,475 (1912); McCoy, U.S. Pat. 1,268,031 (1918); Canadian Pat. 187,645 (1918); see also U.S. Pats. 1,299,846; 1,300,218 (1919); 1,245,363 (1918); re-published Pat. 15,199 (1921); Gudge, U.S. Pat. 1,299,706 (1919); Wells, U.S. Pat. 1,332,860 (1920); Power, U.S. Pat. 1,427,844 (1922).

<sup>5</sup> Rütgerswerke Akt.-Ges., German Pat. 348,063 (1918); *C.* (1922), 11, 748. Lander, British Pat. 17,576 (1915); *Kunstst.*, 7, 332 (1917); Muth, German Pats. 301,926-7 (1915); *Kunstst.*, 8, 70, 72 (1918); German Pats. 302,632 (1916); 305,271 (1917); *C.* (1918), I, 590, 980; U.S. Pat. 1,194,866; *Kunstst.*, 7, 38 (1917); Ellis, U.S. Pat. 1,007,681 (1911); see also Perry, U.S. Pat. 1,302,209 (1919), and Roether, U.S. Pat. 1,414,670 (1922), who proceed in a similar manner.

Cumarone resins are also stated to be used in the manufacture of linoleum,<sup>1</sup> oil-cloth, and similar materials.<sup>2</sup> They are also said to be used as cement<sup>3</sup> for binding linoleum to flooring<sup>4</sup> and so forth. According to Marcusson,<sup>5</sup> high melting qualities are used in the explosives industry, whilst dark qualities are used for bird-lime and for the production of axle grease.

## DETECTION AND INVESTIGATION OF CUMARONE RESINS

The following reactions may be used for the detection of cumarone resin—

**Solubility in Acetone.** All qualities of cumarone resin dissolve in acetone, either completely or with the exception of a very small residue, whilst pitches from coal-tar, lignite-tar, wood-tar and petroleum are only slightly soluble. The reaction is of importance, as pitch residues are occasionally offered as dark cumarone resins.

**Solubility in Petroleum Spirit.** In distinction from aldehyde resins, cumarone resins are freely soluble in petroleum spirit.

**Numerical Characteristics.** Natural resins have usually higher melting points than cumarone resins, and show higher acid, saponification, and iodine values. Moreover, they are optically active, whilst cumarone resins are inactive.

**Saponification.** As cumarone resins are insoluble in alkalis, they can be separated from fatty oils by saponification of the latter,<sup>6</sup> and can also thus be distinguished from acid resins, such as colophony, phenol-aldehyde resins, and so forth.

<sup>1</sup> Koch, U.S. Pat. 1,019,066 (1912); Priest, U.S. Pat. 1,334,049 (1921); U.S. Pat. 1,381,737-8 (1921).

<sup>2</sup> Eichler, U.S. Pat. 1,218,599 (1917); *Kunstst.*, 7, 262 (1917); McCoy, U.S. Pat. 1,245,363 (1918); Schaffer, U.S. Pat. 1,441,605 (1923); Köln-Rottweil Akt.-Ges., German Pat. 419,277 (1922); *C.* (1926), I, 1303; *Kunstst.*, 16, 96 (1926).

<sup>3</sup> McCoy, U.S. Pat. 1,236,190 (1917).

<sup>4</sup> On use as substitute for glue, etc., see F. Lehmann and J. Stocker, German Pat. 278,955.

<sup>5</sup> J. Marcusson, *Chem.-Ztg.*, 43, 109, 122 (1919).

<sup>6</sup> H. Wolff, *Farbenztg.*, 23, 307 (1918), found, however, that considerable quantities of saponifiable products may also be present in cumarone resins, and he developed methods for the separation of such resin acids from fatty oils. On the detection of cumarone resins in varnishes, see H. Wolff, *Farbe und Lack* (1928), 85.

**Heating with Soda-lime.** On heating with soda-lime, phenol-aldehyde resins liberate considerable quantities of phenols, whereas cumarone resins yield traces only.

According to Marcusson the test is carried out, for example, by heating 1 gm. of the resin with 3 to 5 gm. of soda-lime for 2 hours to  $260^{\circ}\text{C}$ . in an oil-bath, and the reaction mixture is then extracted with warm water. If the solution yields a considerable separation of phenols on acidification with mineral acid, a phenolic resin is present. In this case, if a few drops of freshly-prepared diazobenzene solution are added to the solution whilst still alkaline, a red precipitate of an azo-dyestuff is obtained, or an intense red coloration. On the other hand, under the same conditions cumarone resin yields a slight precipitate of resin acids only on adding hydrochloric acid. With diazobenzene solution a weak red coloration is produced.

**Dry Distillation.** On heating cumarone resin it decomposes at  $300\text{--}400^{\circ}\text{C}$ . (See page 244.) On re-distilling the distillate a main fraction is obtained of boiling point  $168\text{--}180^{\circ}\text{C}$ ., in which cumarone and indene may be identified as picrates or bromides. (Cumarone picrate, melting point  $102\text{--}103^{\circ}\text{C}$ .; indene picrate, boiling point  $179.5\text{--}180.5^{\circ}\text{C}$ ., melting point  $98^{\circ}\text{C}$ .; cumarone monobromide, melting point  $39^{\circ}\text{C}$ .; cumarone dibromide, melting point  $86^{\circ}\text{C}$ .; indene dibromide, melting point  $43\text{--}45^{\circ}\text{C}$ .) Natural resins give very small amounts only of the above-described fraction, which obviously will contain neither cumarone nor indene.<sup>1</sup>

The  $170\text{--}180^{\circ}\text{C}$ . fraction may also be tested for cumarone and indene<sup>2</sup> by adding a few drops of strong sulphuric acid. In the presence of these substances a viscous polymerized product is obtained; the reaction is, however, not unambiguous.

**Colour Reaction with Bromine.** When the test is carried out as described below, cumarone resin yields a red coloration, whilst resinolic acids from pontianac, for example,<sup>3</sup> give a

<sup>1</sup> According to R. Weissgerber, *Ber.*, 42, 569 (1909), indene can also be easily isolated as the sodium compound.

<sup>2</sup> H. Wolff, *loc. cit.*

<sup>3</sup> The reaction is of special interest under American conditions in order to detect colorimetrically the adulteration of the pale cumarone resins, which are there valued highly, with natural resins; see C. Ellis, *Synthetic Resins and Their Plastics*, p. 54.



reddish yellow colour, which changes into pure yellow on standing for a prolonged period (24 hours).

1 c.c. of a 10 per cent solution of the resin in chloroform is diluted with a further 6 c.c. of chloroform, after which 1 c.c. of glacial acetic acid is added; 1 c.c. of a 10 per cent solution of bromine in chloroform is then added, after which the liquid must be either shaken or stirred, the vessel closed, and allowed to stand. In the presence of cumarone resin a permanent red coloration is obtained.

**Testing Cumarone Resins.** The methods employed for testing cumarone resins are mainly those of the (German) War Committee for Fats and Oils,<sup>1</sup> which distinguish between numerous qualities on the basis of colour and hardness or consistency.

**Determination of Colour of Cumarone Resins.** COMPARATIVE SOLUTION. For the preparation of the comparative solution, 15 gm. of pure potassium dichromate are dissolved in 1 litre of pure 50 per cent sulphuric acid.

RESIN SOLUTION. To prepare the resin solution, 1 to 1.5 gm. of the resin are weighed into a test-tube, with an exactitude of 0.1 gm. When examining soft or viscous samples, it is advisable to use a small rod of glass or wood, which is tared and weighed with the test-tube.

A quantity of ordinary, purified, water-clear benzole is then measured in a small measuring cylinder, in such amount that 1 c.c. of benzole is used for each 0.1 gm. of resin in the test-tube; the benzole is then poured into the test-tube and the resin dissolved by shaking, with or without warming. In the case of many resins this 10 per cent solution is directly suitable for comparison; in other cases, it must be diluted with benzole until of suitable depth of colour.

COMPARISON. The comparison of the freshly-prepared and shaken solution of the resin with the standard dichromate solution must be effected by comparing the solutions side by side in test-tubes of identical diameter, by transmitted daylight,

<sup>1</sup> See *Kunstst.*, 9, 190 (1919); these directions are still authoritative, partly in extended form. The above information was supplied by the Cumaroneharz-Verband G.m.b.H. (Cumarone Resin Association), Bochum, whom we take the opportunity of thanking.

with the sky as a background, attention being given to depth of colour and not to tint.

The *distinction between the colours*, "brown," "dark," and "black" is effected by observing the transmission of artificial light of about 50 candle-power (from an incandescent electric lamp, spirit- or benzol-heated mantle, or the like) through the freshly-prepared solution contained in a test-tube of 15 mm. bore. During the test the distance of the test-tube from the light source should be about 50 cm. Lateral illumination should be cut off by holding the tube between two fingers, or in a wooden block in which two small opposed slots are cut.

**LIMITING VALUES.** These are given in the table on page 255.

**Determination of Hardness and Consistency.** For hard resins the softening point is determined by the Kraemer-Sarnow method, whilst for soft, viscous, or liquid resins the so-called nail-dipping test is used.

**KRAEMER-SARNOW METHOD OF DETERMINING THE SOFTENING POINT.** For this determination glass tubes are used, about 10 cm. long and of 6 to 7 mm. diameter, the ends of which are cut off smoothly. Into such a tube a glass rod is inserted below, which is also smoothly cut off and which fits it exactly: it is inserted so far that when the tube is held in a vertical position by a clamp a free space of exactly 5 mm. height remains at the top. Meanwhile, about 25 gm. of the resin have been melted on the water-bath, and this is now poured, drop by drop, into the remaining cavity at the top of the tube, and the extruding cap cut smoothly away after cooling. After everything is quite cold the glass rod is withdrawn, and exactly 5 gm. of mercury are poured into the tube: this quantity can easily be measured in a specially graduated vessel. The tube, thus charged, is hung in a beaker containing water at about 15° C., which is contained in a larger beaker also containing water at the same temperature. A thermometer dips into the water in the inner beaker at such a height that its bulb is at the same level as the resin in the tube, and the outer beaker is then heated with a moderate flame in such a manner that the temperature rises by about 1° C. per minute. The temperature

at which the mercury ruptures the layer of resin is the softening point of the sample.

**THE NAIL TEST.** For this test the so-called 5-in. round wire nails are used, known commercially as 23/60 nails, which are 130 mm. long and weigh 23 to 24 gm. The resin to be investigated must be filled into a vessel of a diameter of at least 8 to 10 cm. to a height of at least 15 to 20 cm., and must be maintained at a temperature of exactly 20° C., if necessary by immersion in water at that temperature, in which it must stand for a sufficient time (often for 6 to 12 hours). The nails must also be at the same temperature, and must not be warmed by holding in the hand for any time.

The nail is seized by the head by the thumb and index finger of the left hand, and held vertically over the resin sample, whilst with the right hand a simple wire loop of about 10 mm. diameter is slipped over the nail from below nearly up to its head, to serve as a guide for the nail and maintain it in a vertical position when liberated.

The number of seconds is counted, which elapse between the moment at which the head of the nail is liberated, and that at the nail has sunk so far into the liquid that the head just touches the surface. If the nail test gives a figure of less than 5 seconds, a steam distillation test is to be carried out as follows—

**STEAM DISTILLATION.** 100 gm. of the sample are weighed into a glass retort of 350 to 500 c.c. capacity, and the retort is heated in a bath containing oil or cumarone resin until the bath temperature is 150° C. (It is advisable to add about 50 c.c. of benzene or xylene to prevent frothing over.) A vigorous current of steam, which should be as dry as possible, is then passed through the retort, and heating continued until the temperature of the bath gradually rises to 260–270° C. The total duration of the passage of the steam should be one hour. After cooling, the residue is weighed and gives the direct percentage of resin. If less than 35 per cent of resin is found the sample consists of residues or oils containing cumarone, or substances of that character.

**Classification of Cumarone Resins.** After carrying out the above tests on colour, hardness, consistency and residue, any

# CUMARONE AND ALDEHYDE RESINS

cumarone resin or residue containing cumarone resin can be assigned to one or other of the following classes—

TABLE OF COMMERCIALY RECOGNIZED CLASSES OF CUMARONE RESIN

	<i>Pale</i> 10% solution not darker than 15 gm. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> per litre 50% H <sub>2</sub> SO <sub>4</sub>	<i>Pale Brown</i> 3½% solution not darker than 15 gm. K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> per litre 50% H <sub>2</sub> SO <sub>4</sub>	<i>Brown</i> Artificial light pene- trates 10% solution	<i>Dark</i> Artificial light pene- trates 5% solution	<i>Black</i> Artificial light fails to pene- trate 5% solution
<i>Very Hard</i> Softening point over 50° C.	1	2	3	4	5
<i>Hard</i> Softening point be- tween 40° and 50° C.	6	7	8	9	10
<i>Medium Hard</i> Softening point be- tween 30° and 40° C.	11	12	13	14	15
<i>Soft</i> Softening point be- low 30° C. Immer- sion period in nail test more than 500 sec.	16	17	18	19	20
<i>Viscous</i> Immersion period between 100 and 500 sec.	21	22	23	24	25
<i>Liquid</i> Immersion period less than 100 sec.	26	27	28	29	30
Residues containing cumarone resins	31 27-35% resin contents	32 20-27% resin contents	33 below 20% resin contents	34 <sup>1</sup> 20-40% resin contents. Technically free (not over 1%) of sodium phenolate. Maxi- mum water contents 2%	

The figures denote the classes in which the resins are to be placed in accordance with their consistency and colour.

<sup>1</sup> For Class 34 there are special specifications, which refer to the raw material (in the washing of benzole, toluole, or mixtures of these). There are also stipulations with regard to water contents (maximum 2%), boiling point (a maximum of 10% may distil below 200° C.), naphthalene contents (free from naphthalene as far as possible, maximum 6%), resin contents (up to 40%), and sodium phenolate (not over 1%).

A few further classes have recently been added. Thus, the very hard classes with a softening point between  $50^{\circ}$  and  $55^{\circ}$  C. are further characterized by the suffix /50 to their class number. Resins of softening point between  $55^{\circ}$  and  $60^{\circ}$  C. receive the suffix /55, those of softening point between  $60^{\circ}$  and  $65^{\circ}$  C. the suffix /60, and so forth. The pale classes 1 and 6 are also distinguished from "super-pale" classes. If the colour of a freshly-prepared and shaken 10 per cent solution of these resins in benzene is not darker than a solution of 3 gm. potassium dichromate in 1 litre of 50 per cent sulphuric acid, the resin is assigned to the next stage of paleness, which is indicated by the prefix zero; thus, for example,

01/50, 01/55, 01/60, 01/65, etc.,

and similarly for 06/, but not in classes 11, 16, 21, and 26. If the colour of the freshly-prepared and shaken 10 per cent solution of the resin in benzene is not darker than a solution of 1 gm. potassium dichromate in 1 litre of 50 per cent sulphuric acid, the resin is assigned to a still higher degree of paleness, designated by the prefix 00, for example,

001/50, 001/55, 001/60, 001/65, etc.,

and similarly for 006/, but not in classes 11, 16, 21, and 26. If the colour of a freshly-prepared and shaken 25 per cent solution of the resin in benzene is not darker than the solution of 1 gm. potassium dichromate in 1 litre of 50 per cent sulphuric acid, the resin is assigned to a colour class which is designated by the prefix 000, thus,

0001/50, 0001/55, 0001/60, 0001/65, etc.,

but this does not apply to classes 6, 11, 16, 21, or 26.

If the colour of the freshly-prepared and shaken 50 per cent solution of the resin in benzene is not darker than the solution of 1 gm. potassium dichromate in 1 litre of 50 per cent sulphuric acid, the resin is assigned to the next colour class, designated by the prefix 0000, for example,

00001/50, 00001/55, 00001/60, etc.,

but this does not apply to classes 6, 11, 16, 21, or 26.

Higher degrees of paleness hardly occur in practice.

**Determination of Water.** 100 gm. of the resin are dissolved in 200 c.c. of xylene or of Solvent Benzole (I), and are distilled in a flask until a clear distillate is condensed. The distillate is collected in a measuring cylinder in which the number of cubic centimetres of water are read and correspond to the percentage in the sample. Cumarone resins should be technically free from water.

**Test for Admixed Foreign Matter.** 10 gm. of the resin are dissolved in 100 c.c. purified benzene, and shaken for 2 minutes with 100 c.c. concentrated sulphuric acid in a separating funnel. The liquid is allowed to stand for some time, until separation has occurred, and the acid layer removed and shaken up similarly with a further 50 c.c. of benzene. The benzene solutions are united and evaporated in a weighed distilling flask, the last traces of benzene being removed by heating in a vacuum if necessary. The amount of resin which remains represents that portion of the original sample which is not attacked by sulphuric acid.

After deduction of the water contents, cumarone resins may contain up to about 20 per cent of components soluble in sulphuric acid. If this limit is exceeded it is probable that foreign substances have been added, the exact nature of which requires special investigation.

**Determination of Sodium Phenolate.** 50 gm. of resin are dissolved in about 200 c.c. of benzene in a separating funnel; 300 to 350 c.c. of water are then added and the whole well shaken. The phenolates go into the aqueous solution. After allowing to settle, which requires some time, but takes place satisfactorily, the aqueous solution is withdrawn into a 1 litre flask and the benzene solution again treated with 200 c.c. of water. This treatment is repeated, if necessary, with a similar quantity of water. The presence of phenolate in the washings can be tested with bromine water, or by any other of the various reactions for phenol. The aqueous solutions are then made up to 1 litre, filtered, and the phenol in the filtrate determined by Koppeschaar's method as follows—

10 c.c. of the phenol solution, and 50 c.c. of a potassium bromide-potassium bromate solution (7 gm. potassium bromide and 1.6702 gm. potassium bromate per litre) are introduced

into a bottle with a well-fitting glass stopper; 15 c.c. of 50 per cent sulphuric acid are then added and the whole shaken vigorously. Tribromophenol and tribromophenolbromide separate. After 10 to 15 minutes, 10 to 15 c.c. of potassium iodide solution (125 gm. per litre) are added, the whole shaken, and the liberated iodine titrated after some minutes with N/10 thio-sulphate solution, using starch solution as an indicator.

1 c.c. of N/10 thiosulphate solution corresponds to 0.001934 gm. sodium phenolate or 0.001567 gm. phenol. Any cresol which may be present is calculated as phenol.

The relation between the potassium bromide-potassium bromate solution and the N/10 thiosulphate solution is determined by a blank test.

**Determination of Free and Fixed Sulphuric Acid.** According to H. Wolff,<sup>1</sup> an appreciable proportion of cumarone resins of the most various classes contain on occasion quite considerable quantities of acid constituents. Among 30 resin samples, acid ratios of about 1 to 20 and saponification values of about 1 to 25 were obtained. Apart from free sulphuric acid, water-soluble sulphonic acids are especially frequent constituents. There is also a component insoluble in water, which may be present in the form of alkylsulphuric acid, readily dissociated but insoluble in water,<sup>2</sup> or in the form of absorptively fixed sulphuric acid<sup>3</sup> which is liberated on ageing or by coagulation, for example on treatment with salt solutions. Cumarone resins containing such acid constituents show considerable disadvantages during use. Thus they act as rust promoters rather than as rust preventatives. The occasional thickening of solutions of cumarone resins with basic pigments is also attributed to the presence of such components. It is found that the insoluble, fixed acids are injurious, as well as the water-soluble constituents.<sup>4</sup>

**Free Sulphuric Acid.** According to Wolff, 10 to 20 gm. of the resin are dissolved in 50 c.c. of neutral benzene or xylene and then shaken up repeatedly with warm water; three

<sup>1</sup> *Farbenzeitung*, 22, 917 (1917).

<sup>2</sup> Marcusson, *Chem.-Ztg.*, 43, 110 (1919).

<sup>3</sup> H. Wolff, *Angew.*, 37, 502 (1924).

<sup>4</sup> Marcusson, *loc. cit.*

extractions, each with 20 c.c. of water, are usually sufficient. The extracts are united and filtered. The sulphuric acid is then precipitated with barium chloride at about  $80^{\circ}\text{C}.$  after adding a few drops of hydrochloric acid. A rise of temperature to the boiling point should be avoided, as otherwise the fission of sulphonated substances might liberate further sulphuric acid.

**Water-soluble Fixed Sulphuric Acid.** This can be determined in the filtrate from the above determination by making this alkaline by the addition of soda evaporating, adding a small amount of potassium nitrate and fusing. Sulphuric acid is determined in the melt in the usual manner. The question as to whether the sulphuric acid was present as sulphonic acid or the like, or as free acid, can be settled by titrating the aqueous extract with  $\text{N}/10$  sodium hydroxide solution.

**The Total Sulphuric Acid,** namely, the sum of the free sulphuric acid and the soluble and insoluble fixed sulphuric acid, is determined most simply by saponifying a sample (15 gm.) with alcoholic  $2\text{N}$ — $\text{KOH}$  and melting the residue, for which purpose Marcusson adds a small amount of potassium nitrate. The melt is dissolved in water acidified with hydrochloric acid, the solution filtered from insoluble resin, and precipitated with barium chloride.

In two resins, Wolff<sup>1</sup> found 0.35 and 1.17 per cent of sulphuric acid respectively (expressed as  $\text{SO}_3$ ); in six samples he found water-soluble sulphonic acids in amounts expressed by 0.18 to 1.4 per cent.  $\text{SO}_3$ ; and in ten samples he found sulphonic acids insoluble in water, expressed by 0.09 to 2.1 per cent of  $\text{SO}_3$ .

## ALDEHYDE RESINS

The preparation of aldehyde resins, more particularly of those from acetaldehyde, and of crotonaldehyde and aldol from acetaldehyde, has long been known, and has been the subject of much scientific investigation, which is referred to on page 181 *et seq.* These processes have recently acquired increased importance on account of the development of the chemical industry based on acetylene, as the consequent great

<sup>1</sup> *Farbenzeitung*, 22, 917 (1917).



reduction in the cost of acetaldehyde has led to favourable possibilities of resin production. By improvements in the resin-forming processes on the one hand, and suitable treatment of the soft or liquid resins which are primarily formed on the other, products have been successfully obtained which are hard and non-adhesive. Further improvements in the physical qualities have been achieved by the addition of wax and conversion into the flaky form usual in shellac products. Such products are marketed as "Wacker shellac," or "Syntellac," and, as implied by the names, are intended for use as shellac substitutes.

**Production.** We will first call attention to the fact that although alkalies undoubtedly play the main part as condensing agents in the manufacture of aldehyde resins, attempts have been made to replace them by mineral acids or by salts of acid character.<sup>1</sup> Thus, acetaldehyde (800 parts) is resinified with sulphuric acid (400 parts of 25 per cent acid), by first heating for some hours to 40° C. and then to 100° C. After separation of the acid, the tough mass so obtained is converted into a hard resin by further heating for a considerable period to 150° C. Such products, which may also be obtained, for example, with sodium disulphate, or from paraldehyde, crotonaldehyde, and so forth, are distinguished by low melting points, and are intended for admixture with other resins of higher melting point, in order to render these more fusible. They may also be hardened by melting with metallic oxides or by esterification, or otherwise subsequently treated.

Apart from the above process, all attempts to produce aldehyde resins are based on condensation processes in which the reaction is accelerated by the use of alkalies or agents of alkaline reaction. Here and there condensation processes are referred to in which no condensing agent is used, but in which pressure is employed.<sup>2</sup> Such proposals are probably of no importance apart from questions of patent rights.

As an example of the condensing agents used, 5 per cent of

<sup>1</sup> Consortium für elektrochemische Industrie, G.m.b.H., German Pat. 386,689 (1921); *C.* (1924), I, 1717; British Pat. 187,619 (1922); *C.* (1923), IV, 667; *Kunstst.*, 13, 125 (1923); *I.*, 42 (1924); Swiss Pat. 100,946 (1922); *C.* (1923), IV, 1031; French Pat. 557,614; Canadian Pat. 240,753.

<sup>2</sup> German Pat. 381,720 (1920); see also German Pat. 29,230.

sodium hydroxide<sup>1</sup> or 30 per cent of N-NaOH,<sup>2</sup> both calculated as percentages of the acetaldehyde, may be employed, but the proportion and concentration of the alkaline solution may be varied within wide limits. It is stated that the replacement of alkali hydroxides by alkaline earths results both in reducing the operating costs and in harder final products.<sup>3</sup> The admixture of the acetaldehyde, which is very volatile, with the alkaline liquor must be effected carefully in small portions, with stirring and cooling, and under reflux. The reaction, which is at first exothermic, is later assisted by maintaining a moderate temperature; for example, the batch may be maintained at a temperature of about 100° C. for several hours, during which a viscous mass separates, which may advantageously be removed from the aqueous layer. The product is then slowly heated to 150° C., during which process the volatile products, water and crotonic aldehyde, distil over. The attainable yield is 75 to 80 per cent of the acetaldehyde employed, as very considerable quantities of water are liberated. Oily or viscous, resinous masses remain,<sup>4</sup> which are only converted into hard, solid resins by suitable further treatment.

Thus, for example, the aldehyde resin obtained by the use of the most concentrated possible caustic soda solution, which is plastic or hard in the cold, is treated with superheated steam at about 150° C., which removes the last traces of croton-aldehyde.<sup>5</sup> The mass, which is practically odourless, is then heated to 150–200° C. whilst a current of air or other inert gas is led through it. The influence of high temperatures (below 200° C.) on the properties of the intermediate resin, the so-called "thermal treatment," is of extreme importance.<sup>6</sup> It has been found that prolonged thermal treatment is of advantage, not

<sup>1</sup> German Pat. 381,720 (1920).

<sup>2</sup> German Pat. 393,645 (1921).

<sup>3</sup> Elektrizitätswerk Lonza A.-G., Swiss Pat. 90,868 (1920); *C.* (1922), II, 579.

<sup>4</sup> On the use of such products as substitutes for linseed oil, see Farbenfabriken vorm. Bayer & Co., German Pat. 317,731 (1917); *C.* (1920), II, 450; *Kunstst.*, 10, 21 (1920).

<sup>5</sup> Elektrizitätswerk Lonza A.-G., Swiss Pat. 89,061 (1920); *C.* (1922), II, 209.

<sup>6</sup> Consortium für elektrochemische Industrie, G.m.b.H., German Pat. 381,720 (1920); Swiss Pat. 97,062; *C.* (1923), IV, 667; *Kunstst.*, 13, 125 (1923).

only with the soft resinous products but also at other stages of resin production, as, for example, before the removal of the volatile components by distillation. It is also to be recommended for the various products which are obtained by the processes of purification and after-treatment which we are about to describe. It always results in a higher lustre and increased hardness of the resin, whilst the solubility and fusibility are maintained. (See page 266 *et seq.*)

A further process<sup>1</sup> for the conversion of the liquid or soft primary condensation products into solid, amorphous masses, consists in treating the aldehyde resins with substances of alkaline reaction, whilst finely dispersed by intensive stirring. In this case the presence of a solvent for the aldehyde resin, such as alcohol, assists the action of the alkaline agent.

The use of the aldehyde resins obtained by the processes above described, even though they were very hard, was attended by the very serious disadvantage, compared with the use of natural resins, that the former were more or less attacked by water; when placed in cold water they tended to become coated with an opaque layer, and with boiling water alkali was liberated in the form of a resin soap. It was found possible to secure fastness to water by two distinct processes. According to one process<sup>2</sup> the condensation products obtained with alkali are dissolved in suitable solvents, such as glacial acetic acid or acetone, and then reprecipitated by water. The stage of hardness of the products treated is unimportant, that is, the products purified may consist of the soft, primary condensates or the more or less hardened products which have already been subjected to thermal treatment. The same is true in principle of the second process,<sup>3</sup> according to which the resins are not merely well washed with water, as is usual in any case, but are

<sup>1</sup> Consortium für elektrochemische Industrie G.m.b.H., Swiss Pat. 97,061; C. (1923), IV, 667; *Kunstst.*, 13, 125 (1923); German Pat. 379,832 (1920); C. (1923), IV, 1031.

<sup>2</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 393,645 (1921); C. (1924), I, 2744; Swiss Pat. 100,196 (1922); C. (1924), I, 1717; French Pat. 533,420; C. (1923), IV, 601; British Pat. 182,459 (1922); C. (1923), II, 1000.

<sup>3</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 423,701 (1921); C. (1926), I, 2152; French Pat. 553,420; C. (1923), IV, 601; British Pat. 184,442 (1922).

intensively treated with that liquid in a very fine state of subdivision in a porcelain ball-mill. This wet grinding process is still more effective if the water is replaced by acid. Resin which has been washed in this manner is said to be unaffected even by boiling water. Resins so treated are also specially recommended for use with fatty oils.

The resins produced and purified by these various processes may then be subjected to various subsequent treatments and their properties thus more or less changed.

The various products may be hardened by treatment with metallic compounds.<sup>1</sup> For example, 100 parts of acetaldehyde resin obtained with alkali, of softening point 111° C. (Kraemer-Sarnow) are melted, and 2 per cent of aluminium hydroxide gradually added at a temperature of about 200° C. and the batch vigorously stirred. The product shows a setting point of 150° C.

Greater elasticity, lower melting point, better solubility in alcohol and paler colour are alleged to be imparted to aldehyde resins by the incorporation of hydroxy-acids or of substances containing carbonyl groups.<sup>2</sup> Such additions comprise those of dihydroxystearic acid, ricinoleic acid, dihydroxyabiatic acids,<sup>3</sup> salicyelic acid, castor oil, mesityl oxide, in some cases under pressure, and may be carried out in the presence of a solvent which is afterwards distilled off. The above-mentioned materials may, however, also be added to the raw materials or to the reaction mixture.<sup>4</sup> For example, 30 parts of castor oil are saponified with 75 parts of 2N-NaOH and 100 parts of aldehyde are allowed to flow into the solution so obtained, with stirring and under reflux condensation. The whole is then heated under reflux for five hours to about 100° C., the volatile matter distilled off, and the residue heated to 150° C. The

<sup>1</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 394,946 (1921); *C.* (1924), II, 1138; *Kunstst.*, 14, 139 (1924).

<sup>2</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 422,538 (1922); *C.* (1926), I, 2253; *Kunstst.*, 16, 136 (1926); French Pat. 569,517 (1923); *C.* (1924), II, 1137; *Kunstst.*, 14, 139 (1924).

<sup>3</sup> On production, see German Pat. 426,283.

<sup>4</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 433,853 (1922); *C.* (1926), II, 2500. On the condensation of colophony with aldol or croton-aldehyde in presence of a solvent and of an acid condensing agent, see Farbwerke vorm. Meister, Lucius & Brüning, German Pat. 406,530.

resinous residue in the pan is ground in a ball-mill with three times its weight of 3 per cent acetic acid, after which the powdered resin is filtered, washed, and then heated to 200° C. for some time. The products so obtained<sup>1</sup> can naturally be treated by other methods of purification or after-treatment or hardening, as described above, or by the oxidizing treatment described below.

It is alleged that solubility in borax and soda solutions can be imparted to aldehyde resins by oxidizing treatment, which forms acid groups; this treatment can be applied to the resin in the molten, dissolved or suspended state, but preferably in solution.<sup>2</sup> The oxidation process can be accelerated by the action of suitable catalysts, such as compounds of manganese, chromium, iron, lead, and copper, and also by organic superoxides. Apart from imparting solubility in weak alkalies, the treatment also bleaches and hardens the resins. The oxidized aldehyde resins, which show in other respects the solubility of the ordinary products, may be further hardened by esterification with alcoholates or by interaction with metallic bases or salts.

For example, 10 parts of aldehyde resin are dissolved in 100 parts of glacial acetic acid, and ozonized oxygen is then led through the solution for a considerable time. The colour of the solution becomes paler. The resin is then precipitated by addition of water. The oxidation can also be effected by treating a solution of aldehyde resin in glacial acetic acid with oxygen in the presence of a very small amount of manganese acetate, or a suspension of aldehyde resin in water with oxygen in presence of a small amount of permanganate.

The fact is also of interest that aldehyde resins produced in an alkaline medium can be converted by suitable means into substances which are insoluble in acetone and in most other solvents, and which are also exceptionally fast to high temperatures, having melting or decomposition points of over

<sup>1</sup> On use as linoxyn-like masses for the manufacture of linoleum, etc., see Consortium für elektrochemische Industrie G.m.b.H., German Pat. 434,318 (1924); Canadian Pat. 259,177 (1925); *C.* (1926), II, 2857.

<sup>2</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 395,053 (1921); Austrian Pat. 96,819 (1922); *C.* (1924), II, 1138; British Pat. 185,107 (1922); *C.* (1923), II, 754; French Pat. 554,555; *C.* (1923), IV, 601; Swiss Pat. 100,944; *C.* (1924), I, 1716; Canadian Pat. 240,752; U.S. Pat. 1,489,213.

300° C.; they also withstand the action of hot 30 per cent sodium hydroxide solution and of strong hydrochloric acid to a high degree. Such products are obtained either by prolonged heating under pressure of the aldehyde resins reprecipitated from solution in glacial acetic acid, or by the action of strong sulphuric acid, for example, on the resin, which may suitably be dissolved in glacial acetic acid.<sup>1</sup> Especially pale resins, which are also distinguished by great fastness to light, are obtained by treatment of the original products with halogens or with substances which liberate halogen.<sup>2</sup>

The raw materials for the processes which have been described are more especially acetaldehyde<sup>3</sup> and its polymers, and also aldol and croton-aldehyde. The use of such products as butyr-aldehyde has also been recommended, but the products obtained from these are of no practical importance. On the other hand, it is possible that a certain future importance may be attached to the aldehyde resins which can be obtained from furfural. Resin formation from furfural under the influence of alkalis has been studied by Meunier,<sup>4</sup> and also by Mains and Phillips.<sup>5</sup> Black resins are so obtained, which have promising useful applications for many purposes if the price of the furfural which serves as the raw material should ever be sufficiently reduced. Resinous products can also be produced from furfural in acid solution, in the presence of zinc, for example.<sup>6</sup> The resinification of acrolein, an unsaturated aldehyde, has already been discussed in the General Portion (page 103 *et seq.*), on account of the fact that the reaction depends mainly on polymerization.

<sup>1</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 379,832 (1920).

<sup>2</sup> I. G. Farbenind. A.-G., German Pat. 448,427.

<sup>3</sup> The utilization of acetylene in the presence of suitable catalysts (mercury salts) must also be considered as an application of acetaldehyde; see Consortium für elektrochemische Industrie G.m.b.H., French Pat. 593,338; Austrian Pat. 103,106; *C.* (1926), II, 1791.

<sup>4</sup> French Pat. 472,384; *Kunstst.*, 12, 23 (1922); *Les Matières Grasses* (1916), 4516.

<sup>5</sup> *Chem. Met. Eng.*, 24, 661 (1921).

<sup>6</sup> Vereinigte Chemische Werke, Akt.-Ges., Dr. K. Lüdecke and Dr. L. Mamlock, German Pat. 307,622 (1917); *Kunstst.*, 9, 316 (1919); *C.* (1920), II, 38; on the production of plastic masses from a solution of cellulose esters in furfural by the addition of small amounts of acids, see Ellis-Foster Co. (*C. Ellis*), U.S. Pat. 1,558,442 (1924); *C.* (1926), I, 1334.

PROPERTIES AND APPLICATIONS OF  
ALDEHYDE RESINS

The aldehyde resins are more or less coloured products, partly in leaf form, which are readily soluble in acetone, alcohol, and glacial acetic acid, and completely soluble, although to a lesser extent, in petroleum spirit, benzene, its homologues, turpentine oil, tetraline, dekaline and chlorinated hydrocarbons. During the process of solution the batch should be repeatedly shaken, as otherwise deposits form on the undissolved material, which hinder access of the solvent and consequent solution. In external appearance the aldehyde resin, sold as "Wacker shellac," or "Syntellac,"<sup>1</sup> resembles natural shellac fairly closely. The product is fast to light, odourless, completely harmless (non-poisonous), and permanently soluble. It is supplied both wax-free and with wax. In contrast to natural shellac, the ordinary qualities are very resistant to the action of alkalis, but, as already mentioned, the property of solubility in borax and sodium carbonate solutions, which is so valuable a property of natural shellac, is shared by a special aldehyde resin (oxidized resin). The aldehyde resins differ fundamentally from shellac by the fact that they are not resistant to oil, a circumstance which is, however, not very important, as other synthetic resins, more especially the phenol-formaldehyde resins, are completely fast to oil, and are therefore able to replace shellac in many instances, for example, for electrical insulation.

The various qualities of Wacker shellac which are marketed, and which are intended for various special applications,<sup>2</sup> are stated to have proved satisfactory. Aldehyde resin is used

<sup>1</sup> Dr. Alexander Wacker-Ges. für elektrochemische Industrie, Munich. The following information is based in part on information kindly placed at our disposal by that firm, for which we tender our thanks here.

<sup>2</sup> Wacker shellac "ECW," which forms turbid solutions, as it contains wax, and Wacker shellac "EW," which contains no wax and therefore forms clear solutions, both in leaf form, are suitable for matté polishes, polishes, varnishes, and so forth. Wacker shellac "B," forming turbid solutions, and "C," forming clear solutions, are sold in lump form, are very adhesive, and are suited to the requirements of the electrical industry. Wacker shellac "KR" (clear soluble) in lump form, is suitable for pressed mouldings, cements, primings and oil varnishes; there are many other qualities. (Information from the producers).

for the manufacture of varnishes, polishes, matte varnishes, cements, primings, oil varnishes, and so forth, and for electrotechnical purposes, also, in the form of the qualities soluble in borax and soda solutions, for the production of textile finishes, polishing inks, and so forth.

O. Edelman has compared the insulating properties of Wacker shellac (Quality ECW165 B) and natural shellac.<sup>1</sup> The following results were obtained by measuring the surface resistance<sup>2</sup> of various impregnated materials, being the average results from a large number of determinations.

	Paper	Linen	Silk
	Megohms	Megohms	Megohms
ECW 165 B .	2,350,000	192,300	646,300
Natural Shellac	1,800,000	207,000	517,000

The test for breakdown voltage<sup>3</sup> gave the following figures, in which (I) denotes air-dry soaked strips, and (II) soaked strips heated for 10 hours to 70° C., reduced to 0.1 mm. thickness.

	Paper	Linen	Silk
	Volts	Volts	Volts
ECW 165 B (I) .	3,000	980	2,600
Natural Shellac (I) .	4,950	1,300	3,300
ECW 165 B (II) .	5,600	525	3,000
Natural Shellac (II)	3,940	400	2,200

<sup>1</sup> Communication No. 3-4 of Bayrische Landesgewerbeanstalt, Nürnberg. See *Farbe und Lack* (1925), 54.

<sup>2</sup> Method proposed by the Verband deutscher Elektrotechniker (VDE) with a voltage of 1,000 volts, applied to two metallic knife edges, 10 cm. long and 1 cm. apart. The measurements were made with 66% air saturation and at 25° C. The strips are impregnated twice with a 40% solution, and the measurements were carried out after these had dried for 14 days. Strips which had been further dried for 10 hours at 70° C. gave results which did not differ materially.

<sup>3</sup> The test was carried out between two round disc electrodes with rounded edges, between which the strips were held. The voltages were measured with precision voltage transformers and voltmeters.



The dielectric constants were determined on paper strips, and gave the following mean values<sup>1</sup>—

ECW 165 B	4.58
Natural Shellac	4.80

Wacker shellac is excellently suitable as a substitute for natural shellac, which is much dearer, as a binder in the manufacture of micanite, mikarta-sheets and similar products. If Wacker shellac (Syntellac) B is used in 35 per cent alcoholic solution, plates and moulded masses of any shape can be produced without any difficulty by the usual methods of micanite production.

When preparing moulded articles it is advisable to add 1.5 to 2 per cent of wood oil fatty acid, calculated on the weight of the Wacker shellac. In cases where exceptional strength is required, for example for difficult mouldings, the addition of 10 per cent of calcined magnesia is said to have a favourable effect. This material interacts with the resin in the mould during the heating operation. The temperature to which the masses are exposed is 250° C. in all cases, and the duration of heating 50 minutes. In the production of micanite plates a pressure of 10 kg. to 15 kg. per sq. cm. is applied, and the temperature is maintained at 150° C. during 15 minutes. For the production of "Collector micanite" (pressed micanite) a pressure of 70 kg. per sq. cm. for a period of 50 minutes and a temperature of 160–180° C. are required. Mikarta sheets are produced in the same manner as with natural shellac. Saponified fats are the most suitable lubricants for the moulds. The products prepared as described, are in every way equal in quality to those made with natural shellac as a binder, for example, with regard to appearance, mechanical strength, and more particularly with regard to breakdown voltage.

Wacker shellac is recommended as a substitute for natural shellac for the production of masses to be used for press-moulded articles, such as telephone mouthpieces and wireless fittings. The objects so obtained are only very slightly inferior

<sup>1</sup> A capacity bridge was used with alternating current of 840 periods. A three-plate condenser was formed from the paper strips, between which tin-foil strips were interposed. The measurements were made at ordinary room temperature.

with regard to lustre, strength, and hardness to those produced with natural shellac, which is much more expensive. In general, about 10 per cent more artificial binder is required than is the case with natural shellac. A composition for pressed goods may, for example, consist of 100 parts Wacker shellac KR, about 260 parts kaolin or magnesia, and about 30 parts asbestos fibre or cotton waste or the like; 2 to 5 parts of shellac wax may also be added. The mixture is pressed in the usual manner in heated moulds, preferably at 160–180° C. In the above case, 5 parts of coco-nut oil fatty acid and 1 to 1½ parts of shellac wax are recommended as additions. It is apparently sometimes advisable to mix these additions to the binding agent, and to maintain the molten mixture at 180–200° C. for some time in order to attain as high a softening point as possible.

Wacker shellac (Syntellac) B serves as an excellent adhesive for various purposes. It is an excellent insulator for both heat and electricity, is resistant to moisture, and more resistant to soda, caustic alkalies and similar substances than ordinary shellac. Wacker shellac may be used as an adhesive in the molten condition, for example for uniting electrical insulating materials, and then offers the advantage that it is not so easily “burnt” as natural shellac, but easily withstands temperatures of 200° C. and over. It may also be used as a 55 to 60 per cent spirit solution. From 100 kg. of Wacker shellac B and 83 to 102 litres of about 95 per cent denatured spirit, 170 to 190 litres of an adhesive are obtained, which is used, for example, as a linoleum cement, as an adhesive in stencil-cutting, for uniting the felt to the rollers in wall-paper printing, and so forth.

Various cements may be produced from Wacker shellac KR and various fillers, as the former is an excellent binder for the purpose. The cements are used in brushes, as sealing wax, for fastening the blades of table knives, in the sockets of electric lamps, and for other similar purposes.

Wacker shellacs are also used for polishing, for which a dilute spirit solution of the resin is employed. For matte varnishes a spirit solution, containing about 30 per cent of Wacker shellac ECW, is employed. Such a solution can be mixed with a small percentage of shellac wax, dissolved in benzene or oil,

by which means any required degree of thickening is obtained. Such a solution is also easily incorporated with 1 to 2 per cent of linseed oil, and so acquires an exceptional degree of fluidity. In order to obtain coatings of exceptional hardness, the matte varnish may be mixed with Zapon varnish or similar materials.<sup>1</sup> Wacker shellac matte varnish is, moreover, miscible with matte varnishes prepared from natural shellac, and with solutions of other natural and synthetic resins. The matte varnishes are used in the same manner as those prepared from natural shellac. Paraffin oil, linseed oil, and so forth, may be used for oiling.

A further use of Wacker shellac is as a priming composition, for which 40 per cent solutions of Wacker shellac KR in spirit are recommended. By applying this to wood, masonry, distempered or lime-washed surfaces, metals, and so forth, a priming coating for oil paints, which dries within half an hour, is obtained, which takes the covering coat satisfactorily. The rapid drying power of this material enables much time to be saved, compared with the use of other priming preparations.

The use of spirit solutions of Wacker shellac KR, mixed with red lead, has been proposed as an anti-rusting composition, in place of the usual mixture of oil and red lead. The use of Wacker shellac ECW as a varnish base for paints for ships' bottoms, and for the preparation of anti-fouling compositions, seems to be more promising.<sup>2</sup> The following product, containing 60 per cent of varnish and 40 per cent of pigment, has proved successful for painting ships' bottoms—

		o/o
VEHICLE.	Wacker shellac (Syntellac) ECW	19.7
	Methylated spirit	58.2
	Pine oil .	11.4
	Turpentine	10.7
PIGMENT.	Zinc dust .	7.5
	Zinc oxide	42.5
	Spanish Red	25.0
	Asbestine .	25.0

An anti-fouling composition should contain, for example, 60 per cent of the above body varnish, 27.5 per cent of the above pigment, and 12.5 per cent of poisonous compounds.

<sup>1</sup> The Consortium für elektrochemische Industrie also supplies a colourless liquid, known as Matte Varnish Hardener BP 30.

<sup>2</sup> Regarding such products, see J. Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), pp. 405 *et seq.*

Many of the patents already referred to recommend the use of aldehyde resins for the production of oil varnishes, or of the corresponding oil paints. Aldehyde resin is not, however, directly soluble in linseed oil, but requires, in common with numerous other natural and synthetic resins, to be warmed with the oil for a more or less prolonged period in order to ensure proper incorporation and prevent separation on cooling. On the other hand, the process of "gum running" which is required for copals, and which involves considerable loss of weight, is not required for aldehyde resins.

For the production of oil varnishes, Wacker shellac is recommended, and is dissolved in linseed oil at 300° C. It is advantageous to heat the mixture further for a short period to 330–350° C. The varnishes are finished in the usual manner.<sup>1</sup>

Further details will be found in the patent literature,<sup>2</sup> according to which 3 kg. of aldehyde resin are melted in a pan, after which 5 litres of linseed varnish oil are slowly stirred in at 150–300° C. The mixture is then maintained at this temperature until a sample remains perfectly transparent on cooling. This requires from 2 to 15 hours, according to the melting point of the resin which is used.

In the same patent specifications the recommendation is made to facilitate the solution of aldehyde resins in fatty oils by the addition of natural resins soluble in oil, followed by heating for a considerable period to 150–300° C. It is alleged that in this manner oil varnishes and enamels are obtained which are durable and weatherproof.

The aldehyde resins obtainable with hydroxy-acids or ketones are recommended for use as linoleum-like materials for the production of linoleum, artificial leather, and so forth.<sup>3</sup> Aldehyde resin may be vulcanized by immersion in a solution of sulphur chloride in carbon disulphide.<sup>4</sup> It is then insoluble in most solvents, and elastic, but no longer plastic.

<sup>1</sup> See J. Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), pp. 357 *et seq.*

<sup>2</sup> Elektrizitätswerk Lonza A.-G., German Pat. 372,103 (1921); Swiss Pats. 88,191, 89,243 (1920); C. (1921), IV, 810, 1069; *Kunstst.*, 12, 14, 22 (1922).

<sup>3</sup> Consortium für elektrochemische Industrie G.m.b.H., German Pat. 434,318 (1924); Canadian Pat. 259,177 (1925); C. (1926), II, 2857.

<sup>4</sup> Elektrizitätswerk Lonza A.-G., Swiss Pat. 89,064 (1920); *Kunstst.*, 13, 45 (1923).

## CHAPTER XII

### PHENOL-ALDEHYDE RESINS

THE phenol-aldehyde condensation products of resinous character, which were introduced technically about 25 years ago, have acquired an exceptionally large field of application, which is still steadily extending. This is mainly due to the fact that the method of production of these substances is capable of very wide variation, and products can consequently be obtained especially adapted to very varying requirements.

As already explained (page 142 *et seq.*), an essential difference exists between the interaction of phenols with formaldehyde on the one hand, and with all other aldehydes on the other; this difference is of technical importance mainly owing to the fact that certain products produced with formaldehyde possess the distinctive capacity for being "hardened," a process which is comparable with the ripening process of natural resins, but which can be effected within very short periods by suitable means, for example by heating. Apart from a few exceptions, such as furfural and acrolein, the phenol condensation products of which are of no serious technical importance for practical reasons, the other aldehydes produce products which are either devoid of the capacity for being hardened, or which possess it to a quite insufficient degree only, such as acetaldehyde.

In the patent literature, which is very extensive but furnishes almost the only literature dealing with these products, this difference is not always pointed out. Very frequently, "aldehydes" in general are mentioned as components for the condensation with phenols, whereas it is quite clear, from general considerations, that formaldehyde or its equivalents are actually intended. In actual fact, the formaldehyde-phenol condensation products form by far the most important class of these products.

In order to obtain a clear view of the methods of production of these synthetic resins and of the properties and applications

of the various products, the following description will be arranged according to the aldehyde employed in each case. Thus formaldehyde, furfural, acrolein, acetaldehyde and other aldehydes and ketones will be considered in turn as the characteristic components. More general processes of condensation will be specially dealt with in the formaldehyde section, so that the other sections will be exclusively confined to the consideration of the respective aldehydes and their products.

In 1872 to 1874, A. von Baeyer<sup>1</sup> and his pupil, E. ter Meer,<sup>2</sup> discovered that resinous substances are formed during the reaction between phenols and formaldehyde or methylal. These observations were of no practical importance at that time, as formaldehyde was a substance which was much too difficult to obtain. Formaldehyde only became a product obtainable at a reasonable price through the technical development of the oxidation of methyl alcohol at the end of the eighties of the last century. This caused attention to be again directed to the resinification processes just referred to. The first investigators to take a renewed interest in these reactions were Kleeberg,<sup>3</sup> Tollens and Hosaeus,<sup>4</sup> and Abel.<sup>5</sup> A proportion of formaldehyde greatly exceeding the equimolecular proportion was ordinarily interacted with various phenolic substances, such as phenol, resorcin, pyrogallol, gallic acid and phloroglucin, in the presence of strong acids, such as concentrated hydrochloric acid, sulphuric acid, and so forth, and amorphous products were obtained, which were completely insoluble in ordinary solvents, and which, with the exception of the product from gallic acid, were also insoluble in solutions of alkalies and ammonia. On heating to a high temperature they did not fuse, but simply carbonized. These products evidently corresponded with those now obtained as end-products of the hardening process (resites). Hosaeus and Abel moderated the reaction by avoiding as condensing agents the mineral acids which are extremely active. Thus, from  $\beta$ -naphthol and formaldehyde,

<sup>1</sup> *Ber.*, 5, 1095 (1872).

<sup>2</sup> *Ber.*, 7, 1200 (1874).

<sup>3</sup> *Ann.*, 263, 283 (1891); 264, 351 (1891).

<sup>4</sup> *Ber.*, 25, 3212 (1892).

<sup>5</sup> *Ber.*, 25, 3477 (1892).

in presence of acetic acid, Hosaeus obtained a crystalline product, soluble in alcohol, acetone, and ether, namely,  $\beta$ -dinaphtholmethane. In a similar manner Abel obtained crystalline products from  $\beta$ -naphthol and menthol, whilst from  $\alpha$ -naphthol and guaiacol he was only able to obtain soluble oils or amorphous masses (resins). Similar observations on the interaction of formaldehyde with phenols in the presence of very small amounts of mineral acid and when using the theoretical quantity of formaldehyde, were communicated by N. Caro, L. Kahl, Coster van Voorhout and Trautenberg.<sup>1</sup>

Even these few observations plainly showed the influence exerted by the condensing agent (acid) and by the proportion of formaldehyde. Both these factors played an important part in the technical development of these processes, which commenced at the beginning of the present century. Three aims may be distinguished, according to the purposes for which the various resins were intended. At first attempts were made to develop the process in such a manner as to obtain a product which might serve as a shellac substitute, more particularly for use in spirit varnishes and polishes. The object was, therefore, to obtain a product which dissolved easily in alcohol, and the solubility of which did not decline through further transformation on storage. It was also of importance to moderate the violent reaction, which led to the production of insoluble and infusible masses, in order to obtain the primary resinous substances, which are soluble and fusible and which could then be further transformed as desired. Finally, attempts were made to convert the ordinary fusible phenol-formaldehyde condensation products, which are insoluble in hydrocarbons and fatty oils, in a technically feasible manner into products soluble in those solvents, in order thus to place the use of these products in the varnish industry on a broader basis, and to obtain copal substitutes for the production of oil varnishes.

As a result of these attempts, three main classes of phenol-formaldehyde condensation products have been developed, namely:

<sup>1</sup> On the historical development, see L. H. Baekeland, *Chem.-Ztg.* (1909), 317, 326, 347, 358, 1268; (1912), 1245; H. Lebach, *Angew.* (1909), 1598; *Chem.-Ztg.* (1913), 733, 750; see also Ullmann, *Encyclopaedia*, II, 129; Vli 297; Bottler, *Kunstharze*, München (1919); etc.

1. Shellac substitutes (novolacs);
  2. Hardening resins (resoles);
  3. Copal substitutes;
- to which we will add a further category.
4. Sundry other products.

### SHELLAC SUBSTITUTES (NOVOLAKS)<sup>1</sup>

Phenol-formaldehyde condensation products were first technically applied as shellac substitutes, stimulated by the rising price of shellac. Although a perfect substitute was at first out of the question, the new phenolic resins showed an astonishing similarity to natural shellac, especially with regard to solubility, being also soluble in alcohol and insoluble in hydrocarbons and fatty oils, so that a wide field was open to them in the varnish industry. As the quantities required were quite considerable, it is comprehensible that strenuous endeavours were made to endow the substitutes with all qualities required for spirit varnish production, more especially with fastness to light and freedom from odour. In the course of time these aims were in fact achieved.

Certain difficulties were met in the attempt to imitate another essential property of shellac, namely, its capability of being peptonized by weak alkalies, such as borax or ammonia, a property which is largely exploited for the production of inks, washes, finishes, and so forth. The ordinary phenol-formaldehyde condensation products of the character of novolak are certainly soluble in strong alkalies, but not in alkali carbonates, borax, or ammonia. Attempts have recently been made to overcome this disadvantage by supplying the phenol component with acid groups before combination, or by treating the actual resins with suitable reagents.

Phenol-formaldehyde condensation products of the resole class have also been used as shellac substitutes, for which purpose the solubility relations of the so-called initial products are entirely suitable; the main application of these products as shellac substitutes is, however, rather in their application to

<sup>1</sup> On the development of these products see L. H. Baekeland, *Chem.-Ztg.* (1909), 857.



electrical appliances than as spirit varnishes. In this latter field in particular the use of natural shellac has been greatly reduced, and it may be said that without phenolic resins of the resole class the development of modern electrotechnology would have been impossible.

It may be broadly maintained that novolak products are to-day no more extensively used as varnishes than they were in 1913, according to the consumption ascertained by H. Lebach.<sup>1</sup> Apart, perhaps, from certain products soluble in benzole, petroleum spirit and oil, which have been especially developed as copal substitutes (see page 364 *et seq.*), the true technical value of phenol-formaldehyde condensation products is associated with resoles and resite products. For this reason we will dispense here with a general description of the raw materials required for novolak production, which are fundamentally identical with those required for resoles. This is further justified by the fact that for the production of novolak the effect of any variations on the character of the raw materials is relatively unimportant,<sup>2</sup> whereas any such differences are of fundamental importance in the manufacture of resoles. (See page 287 *et seq.*)

**Production.** The first process for the production of a shellac substitute from phenol and formaldehyde was invented by L. Blumer,<sup>3</sup> who used organic hydroxy-acids, such as tartaric acid, as condensing agents.

135 parts by weight of tartaric acid are dissolved with gentle warming in 150 parts by weight of 40 per cent formaldehyde solution in a lead-lined, double-walled vessel; 195 parts of pure, commercial carbolic acid are then added, and the mixture carefully heated until the commencement of the reaction, during which heat is liberated which maintains the mixture at the boil for about 10 minutes. The crude resinous

<sup>1</sup> Chemiker-Ztg., (1913), 733. Novolak resins have recently been used to an increasing extent as additions to cellulose ester varnishes.

<sup>2</sup> In so far as any such variations are of consequence, they are dealt with in the description of the process.

<sup>3</sup> German Pat. 172,877 (1902); *C.* (1906), II, 724; *Kunstst.*, 2, 164 (1912); British Pat. 12880 (1902); *Chem-Ztg.*, 27, 1010 (1903); Friedländer, *Fortschritte der Teerfarbenfabrikation*, VIII, 1343; British Pat. 6823 (1903); French Pat. 329,982.

product then floats on the surface. It is removed, placed in hot water and freed from any adherent phenol or formaldehyde by boiling with a small amount of ammonia. The mass is then poured into cold water, after which it solidifies. A resin produced in a similar manner from 155 parts tartaric acid, 150 parts formaldehyde solution, and 290 parts  $\alpha$ -naphthol no longer melted in hot water, and had therefore to be purified in powdered form.

The products are stated to be improved in quality by subsequent treatment with oxidizing agents, such as persulphates or perborates.<sup>1</sup>

Other processes show that other acids are advantageous as condensing agents, such as sulphurous acid (which promotes a quiet reaction, as compared with HCl or H<sub>2</sub>SO<sub>4</sub>, and also a paler product,<sup>2</sup>) and that bases or salts,<sup>3</sup> or substances such as glycerine mono- or di-chlorhydrin,<sup>4</sup> may be used and yield better results in some cases than acids. The action of a condensing agent may also be modified, for example, by interrupting the action of acids at a certain stage of the process by adding hydrosulphites or alkali salts of formaldehyde sulphonylic acid.<sup>5</sup> The production of insoluble products is thus avoided. The combination of various condensing agents has also been proposed, such as a preliminary condensation with acid agents and the addition of fresh quantities of phenol and formaldehyde together with basic reagents, followed by further condensation;<sup>6</sup> the action of limited quantities of mineral

<sup>1</sup> L. Blumer, German Pat. 217,560 (1908); *Frdd.*, IX, 1119; *C.* (1910), I, 588; *Kunstst.*, 2, 10 (1912). On treatment of the products with hydrogen, by which harder resins of higher melting point are alleged to be produced, see A. Koch, German Pat. 354,697 (1920); *C.* (1922), IV, 441; *Frdd.*, XIV, 1135; with hydrogen sulphide, G. Brunn, Austrian Pat. 88,473; *C.* (1923), II, 531; *Kunstst.*, 13, 57 (1923).

<sup>2</sup> L. Sarason, German Pat. 219,570 (1908); *C.* (1910), I, 974; *Kunstst.*, 2, 164 (1912); *Frdd.*, IX, 1115.

<sup>3</sup> Knoll & Co., German Pat. 219,209 (1907); *C.* (1910), I, 973; *Kunstst.*, 2, 165 (1912); British Pat. 28,009 (1907).

<sup>4</sup> Bayer & Co., German Pat. 237,786 (1910); *Frdd.*, X, 1052; *C.* (1911), II, 920; U.S. Pat. 1,039,858.

<sup>5</sup> Bayer & Co., German Pat. 234,744 (1910); *C.* (1911), I, 1769; *Kunstst.*, 1, 255 (1911); 2, 10 (1912); *Frdd.*, X, 1054; U.S. Pat. 1,039,859 (A. Weindel).

<sup>6</sup> Kulas and Pauling, German Pat. 414,959 (1920); British Pat. 159,494 (1920); *C.* (1921), IV, 133; U.S. Pat. 1,414,139; Canadian Pat. 213,402; French Pat. 540,297; Austrian Pat. 100,049; Swiss Pats. 94,616, 100,402; see also German Pats. 429,033, 431,619.

acid on the condensation product obtained in an alkaline medium has also been proposed.<sup>1</sup> Phenols and trioxymethylene may also be condensed without condensing agents, forming exceptionally pale resins which are unusually fast to light.<sup>2</sup>

Certain other proposals proved more important than any of these and acquired greater practical importance.

It was recognized to be advantageous to supplement the usual washing process by a treatment with steam or toluene vapour. The use for this purpose of vapours of substances which dissolve the resin, such as alcohol, has also been proposed.<sup>3</sup>

It has also been found that the use of o-cresol more easily leads to the production of odourless resins than that of other phenols, and that its condensation with formaldehyde may be effected by acids,<sup>4</sup> salts,<sup>5</sup> or bases.<sup>6,7</sup> m-Cresol, which is much more reactive than any other phenol (see page 293) is stated also to yield resins distinguished by freedom from odour, which are, moreover, stated to be exceptionally pale and hard.<sup>8</sup>

Attempts were also made to impart improved mechanical properties to the products by suitable additions.<sup>9</sup> This seemed to be a promising endeavour, as the elasticity of coatings of natural shellac is mainly ascribed to the presence of natural

<sup>1</sup> Bakelite G.m.b.H., R. Hessen, German Pat. 340,990 (1920); *C.* (1922), II, 39; *Frdl.*, XIII, 645; British Pat. 159,461 (1921); *C.* (1921), IV, 132; French Pat. 531,467; *C.* (1922), II, 704; Swiss Pat. 94,231; *C.* (1923), II, 411.

<sup>2</sup> F. Pollak, German Pat. 310,894 (1911); *C.* (1919), II, 428.

<sup>3</sup> Knoll & Co., German Pats. 219,209 (1907); *C.* (1910), I, 973; 219,728 (1908); *C.* (1910), I, 1075; *Frdl.*, IX, 1121; see also British Pat. 28,009 (1907); French Pat. 395,657; also A. A. Drummond, British Pat. 274,581; *C.* (1928), II, 497.

<sup>4</sup> F. Bayer & Co., German Pat. 201,261 (1907); *Frdl.*, IX, 1116; *C.* (1908), II, 1752; Austrian Pat. 38,663; Swiss Pat. 40,639; British Pat. 26,317 (1907); French Pat. 384,425 (1907); Gentsch, U.S. Pat. 924,449 (1909); see also Baekeland, U.S. Pats. 1,306,681 (1919); 1,401,953 (1922), who recommends the products as plasticisers for other hardening phenolic resins.

<sup>5</sup> Knoll & Co., *loc cit.* 21.

<sup>6</sup> L. Blumer, German Pat. 206,904 (1907); *C.* (1909), I, 965; *Kunstst.*, 2, 165 (1912); advantageously in the absence of air, *Frdl.*, IX, 1118; Austrian Pat. 41,480.

<sup>7</sup> On condensation without condensing agent, but under pressure, and on a resin so produced, see Aylsworth, U.S. Pat. 1,111,287.

<sup>8</sup> *Chem. Fabr.*, K. Albert and L. Berend, German Pat. 301,374 (1913); *C.* (1919), IV, 918; *Frdl.*, XIII, 650; see also German Pat. 304,384 (1913); *C.* (1919), IV, 1053; *Frdl.*, XIII, 652.

<sup>9</sup> See the results of the investigations of the Wiener Versuchsanstalt für chemische Gewerbe (Vienna Research Station for Chemical Industry).

wax. Moreover, such additions sometimes enable the cost of the product to be reduced. The following additions have been proposed: vinyl derivatives<sup>1</sup>, resin acids or resins (especially colophony<sup>2</sup>), casein<sup>3</sup>, aldoses,<sup>4</sup> and also substances which simultaneously act as condensing agents, such as natural resins and balsams, tars and so forth,<sup>5</sup> saponifiable fatty oils, waxes or fatty acids of high molecular weight<sup>6</sup> (products so produced being marketed as "Albertol" shellacs), camphor and ethereal oil.<sup>7</sup> A shellac substitute is also stated to be obtained by the acid condensation of phenol with formaldehyde, with the addition of starch hydrolyzed by nitric acid, stearine, and resin.<sup>8</sup> A similar elasticizing effect is produced by the use of formaldehyde-glycerine condensation products, such as formal-glycerine, in place of glycerine itself,<sup>9</sup> and also by the use of components prepared from fatty oils and phenols.<sup>10</sup>

During recent years less work has been done on the development of processes for the production of novolak resins. This is

<sup>1</sup> Plausons Forschungsinstitut G.m.b.H., German Pat. 364,045 (1918); *Frddl.*, XIV, 1167; U.S. Pat. 1,451,834; British Pat. 156,151 (1920); *C.* (1921), II, 743; according to German Pat. 352,003 and 436,445; *C.* (1922), IV, 157; (1927), I, 190, Meilach, Melamid and A. Riebeck'sche Montanwerke obtain ethers by subsequent treatment of the initial products with allyl or vinyl halides in alkaline solution, some of which may be used as substitutes for fatty drying oils.

<sup>2</sup> Sarason, German Pat. 193,136 (1906); *C.* (1908), I, 1002; *Frddl.*, VIII, 1347; Lingner, French Pat. 386,002 (1908).

<sup>3</sup> H. Kühl, German Pat. 280,648 (1913); *C.* (1915), I, 106; *Frddl.*, XII, 583; *Kunstst.*, 5, 9 (1915); Nakaniski, Japanese Pat. 34,922 (1919); 31,912 (1919); see also Kühl, *Chem. Ind.*, 37, 559; *C.* (1914), II, 1486; *Kunstst.*, 5, 196 (1915); Berend, *Farbenzeitg.*, 20, 411; *C.* (1916), II, 1201; K. Albert, L. Berend, U.S. Pat. 1,040,850; French Pat. 436,720.

<sup>4</sup> A. Bau, British Pat. 218,054 (1923); *C.* (1926), II, 1474; *Kunstst.*, 16, 254 (1926).

<sup>5</sup> K. Albert, L. Berend, German Pat. 254,411 (1910); *C.* (1913), I, 351 *Frddl.*, XI, 849; French Pat. 441,547 (1912); British Pat. 1,269 (1912); Swiss Pat. 72,631 (1916).

<sup>6</sup> K. Albert, L. Berend, German Pat. 269,659 (1911); *C.* (1914), I, 592 *Frddl.*, XI, 852; *Kunstst.*, 4, 172 (1914).

<sup>7</sup> Dr. J. Perl & Co., German Pat. 396,510 (1919); *Frddl.*, XIV, 1148; *C.* (1924), II, 1411; *Kunstst.*, 14, 156 (1924).

<sup>8</sup> E. Noa, German Pat. 237,743 (1908); *Frddl.*, X, 1055; *C.* (1911), II, 1294 French Pat. 419,061; *Kunstst.*, I, 91, 437 (1911); 2, 10, 165 (1912).

<sup>9</sup> Les Produits Chimiques de Croissy, Ltd., German Pat. 210,012 (1907) *Frddl.*, IX, 1117; *Kunstst.*, 2, 164 (1912); *C.* (1909), II, 81; Swiss Pat. 43,633 *Kunstst.*, I, 313 (1911); 2, 94 (1912); U.S. Pat. 906,219; *Kunstst.*, 2, 95 (1912) British Pat. 16,528 (1908); French Pat. 390,713.

<sup>10</sup> Bakelite Corp., L. C. Byck, U.S. Pat. 1,590,079 (1923); *C.* (1926), II, 1793.

due to the fact that the demand for these products, which was always limited, has been still further reduced by the increasing competition of cellulose esters. In addition, the various processes which have been developed for the production of the far more important hardening resins of the resole class, which have resulted in advances, for example, in the fastness to light of those products, are also applicable with but little modification to the production of the shellac-like products. We may, therefore, refer to the section on the production of resol resins for information on further developments in novolak production.

We must, however, refer here to the endeavours which have been made to reduce the proportion of formaldehyde to phenol, in which respect the choice of condensing agent has been found to be of considerable influence.<sup>1</sup> It has been found that if acid condensing agents are used, such as acids of all kinds and acid salts, the reaction proceeds very far if but little more than 1 mol. of formaldehyde is present per 2 mol. of phenol, and that a fusible and soluble resin is thus produced in a very constant time of reaction. On the other hand, as the proportions approach 1 mol. of phenol to 1 mol. of formaldehyde the products acquire the property of hardening to an increasing extent, and on this tendency both the concentration and strength of the acid and the time of reaction have a predominant influence.

Bases and salts which hydrolyse with production of a basic reaction are not generally found to be suitable for the production of novolak resins, with the exception of the processes based on the use of o-cresol (see page 278), as in contrast to acids and acid salts, even traces of basic products affect the reaction in such a manner that so-called phenol-alcohols are produced from molecular proportions of phenol and formaldehyde.<sup>2</sup> As this reaction also occurs in the presence of excess of phenol, for example, when 2 mol. of phenol are present per molecule

<sup>1</sup> L. H. Baekeland, *Chem.-Ztg.* (1909), 317, 326, 347, 358; *idem.*, 857; *idem.* (1912), 1945.

<sup>2</sup> See Lederer, *J. prakt. Chem.* (2) 50, 224 (1894); Manasse, *Ber.*, 27, 2408 (1894); *Farbenfabr. vorm. Bayer & Co.*, German Pat. 85,588; *Chem.-Ztg.* (1896), 275; Manasse, U.S. Pat. 526,186 (1894).



of formaldehyde, more particularly with regard to solubility in alcohol. Substances of this character have been known for many decennia under the name of "saliretines."<sup>1</sup> The formation of such compounds may be mainly ascribed to anhydriization processes, and may play some part in the processes first referred to above.<sup>2</sup> The fact that a certain hardening capacity is present is shown by the disappearance of the solubility in alcohol when phenol-alcohols are heated for a considerable time to temperatures over 100° C.<sup>3</sup>

Finally, we must refer to processes by which phenol-formaldehyde condensation products are produced which are soluble in weak alkalis, such as borax or sodium carbonate, and which are specially intended for use as textile finishes, and so forth. This solubility is attained<sup>4</sup> by replacing the phenols, wholly or partially, by phenolcarboxylic acids, such as salicylic acid and p-hydroxybenzoic acid,<sup>5</sup> phenol-ether-carboxylic acids, such as o-methoxybenzoic acid<sup>6</sup>, arylhydroxyacetic acids,<sup>7</sup> or other arylhydroxy-fatty acids.<sup>8,9</sup> The substances just mentioned are condensed with formaldehyde (usually less than 1 mol.) in the

<sup>1</sup> Piria, *Ann.*, 56, 37 (1845); Meyer-Jacobson, *Lehrbuch*, II, 1, 468.

<sup>2</sup> On the production of substitutes for natural resins by heating phenol-alcohols *in vacuo*, see Fabriques de Produits de Chimie Organique De Laire, German Pat. 189,262 (1905); *C.* (1907), II, 2002; British Pat. 15,517 (1905); Belgian Pat. 192,590 (1906); French Pats. 350,180; 361,539; turpentine oil and camphor oil, and so forth, are referred to as solvents. On the production of a synthetic resin by heating a mixture of o- and p-hydroxybenzylalcohol with acids, see Farbw. vorm. Meister, Lucius & Brünig, German Pat. application, F. 43,811, Class 22h, of 21st. October, 1918.

<sup>3</sup> De Laire, German Pat. 189,262 (1905); *C.* (1907), II, 2002; *Frdl.* VIII, 1345; F. Raschig *Angew.* (1912) 1946; regarding hardening see Baekeland U.S. Pat. 1,033,475, 1,146,045; *Kunstst.*, 5, 239 (1915); Belgian Pat. 213,576; French Pat. of addition 11,628; U.S. Pat. 1,187,232 (in the presence of bases); *Kunstst.*, 6, 298 (1916).

<sup>4</sup> See also G. Cohn, *Chem.-Ztg.* (1916), 725; On Artificial Resin Acids.

<sup>5</sup> Farbw. vorm. Meister, Lucius & Brünig, German Pat. 339,495 (1919); *Frdl.*, XIII, 656; *C.* (1922), IV, 51; German Pat. 357,757 (1920); *Frdl.*, XIV, 1159; *C.* (1922), IV, 956.

<sup>6</sup> The same, German Pat. 357,758 (1920); *Frdl.*, XIV, 1159; *C.* (1922), IV, 956; German Pat. 358,401 (1920); *Frdl.*, XIV, 1160.

<sup>7</sup> The same, German Pat. 364,040 (1919); *Frdl.*, XIV, 1170; *C.* (1923), II, 921; German Pat. 371,147 (1920); *Frdl.*, XIV, 1171; German Pat. 439,962; *C.* (1927), I, 1531.

<sup>8</sup> The same, German Pats. 371,148-9 (1920); *Frdl.*, XIV, 1172-3; *C.* (1923), IV, 601.

<sup>9</sup> The same, German Pat. 386,733 (1920); *Frdl.*, XIV, 1163; *C.* (1924), I, 2744; *Kunstst.*, 14, 107 (1924).

usual manner, and in some cases by heating under pressure.<sup>1</sup> Resins of similar solubility are obtained on treating fusible, resinous products of the condensation of phenols and formaldehyde with sulphuric acid,<sup>2</sup> or with halogenated fatty acids.<sup>3</sup> The resins soluble in borax and so forth may also be melted together with natural resins, after which the mass may be further hardened by treatment with oxides and so forth.<sup>4</sup> The products form varnishes which give non-adherent coatings. The resins obtained by the processes described above are not only soluble in borax, but also in alcohol and acetone, and are insoluble in hydrocarbons.

**Properties and Applications.** The products known as shellac substitutes are marketed under various trade names, such as Laccain, Novolak, Abalak, Sibolite, Metakalin, Issolin, Bucheronium, and Albertol shellac, some of these being supplied in more than one quality. They are completely colourless, yellow or brown products, having practically the same solubility in various solvents as natural shellac, with the exception that certain special varieties only are soluble in borax. They are, of course, all soluble in methylated spirit, forming clear spirit varnishes, ready for immediate application. Most of them are practically insoluble in hydrocarbons, in which some are absolutely insoluble. They are unaffected by mineral oils, such as transformer oil. They are also resistant to water, acids, ammonia, and other weak alkalies, but not to strong alkalies such as alkali hydroxide solutions. Some of them are very hard and have high melting points (up to 150° C.).<sup>5</sup> They are also characterized by capacity for receiving a high polish, spreading power and high lustre of the coatings. They suffer under the disadvantage for some purposes that the coatings have not the same elasticity as those produced from shellac. Otherwise the excellent qualities already mentioned, together with capacity

<sup>1</sup> The same, German Pat. 358,401 (1920); 371,149 (1920).

<sup>2</sup> L. Levy, British Pat. 273,756.

<sup>3</sup> Farbzw. vorm. Meister, Lucius & Brüning, German Pat. 391,539 (1920); *Frddl.*, XIV, 1165; *C.* (1924), II, 1028; see also I. G. Farbenindustrie A.-G., German Pat. 439,962; *C.* (1927), I, 1531; German Pat. 449,276; *C.* (1927), II, 2237. The products are known as "Synthetic resin E."

<sup>4</sup> The same, German Pat. 422,910 (1921); *C.* (1926), I, 2254.

<sup>5</sup> On molecular weight, see L. H. Baekeland, *Chem.-Ztg.* (1909), 557.



for admixture with pigments, render these shellac substitutes valuable materials for the varnish industry, which are able to replace shellac in very many cases. The faults of which complaint was frequently made formerly, such as phenolic odour and unsatisfactory fastness to light, may be said to be now overcome.<sup>1</sup>

The spirit varnishes are mainly used for the production of polishes, for which purpose producers must comply with certain precautions in order to obtain satisfactory results. These resins may be dyed with aniline dyestuffs as desired. They may also be employed incorporated with pigments, and so forth. Latterly, resins of the novolak class have also acquired some importance as additions to cellulose ester varnishes, in order to improve the coats obtained with these, with regard to lustre, body, adhesion and stability.

### HARDENING RESINS (RESOLES)<sup>2</sup>

The "hardening resins" of the phenol-aldehyde class, which were introduced about the year 1907, are used as shellac substitutes for varnishing purposes in special cases only, although in the electrical industry they have replaced natural shellac practically completely.<sup>3</sup> Their solubility especially in spirit, enables them to be widely used as adhesives for the most various materials. Their fusibility has led to their employment for castings. The hardening process to which all these products are susceptible, converts them into extremely resistant masses, which are widely used, both in the electrical industry<sup>4</sup> and in the various industries which use plastic masses for fancy goods, and so forth.

<sup>1</sup> Fonrobert, *Chem.-Ztg.*, 46, 513 (1922); 47, 829 (1923); *Kunstst.*, 13, 111 (1923).

<sup>2</sup> On the technical development see L. H. Baekeland, *Chem.-Ztg.* (1909), 317, 326, 347, 358; (1912), 1245; H. Lebach, *Angew.* (1909), 1598; *Chem.-Ztg.* (1913), 733, 750; also Ullmann, *Enzyklopädie*, II, 129; VII, 297; Bottler, *Kunstharze*, München (1919); C. Ellis, *Synthetic Resins and Their Plastics*, New York (1923).

<sup>3</sup> It should be noted, however, that natural shellac is again being used for certain special electrical applications. It is also preferred to resoles for the production of gramophone discs.

<sup>4</sup> The annual consumption, for this purpose only, in Europe and America during 1925 was estimated to be at least 4,000 tons, and has probably increased since; H. Lebach, *Angew.*, 38, 1092 (1925).

The so-called "hardening process," the capacity of undergoing which is the characteristic property of these products, depends on the fact that when heated they are more or less rapidly transformed into completely neutral, odourless, infusible, and insoluble products, a process which is to some degree analogous to the ripening of copals.<sup>1</sup> It is a very important feature of this process that it can, if required, be carried out very rapidly, for example, in the course of a few minutes, and by the application of temperatures of about 100° C. which do not affect even the most sensitive fillers or supporting bodies. Regarding the details of the process, see page 142 *et seq.*

**Production.** The raw materials used for the production of phenol-formaldehyde resins are primarily technical carbolic acid, which is a mixture of the three isomeric cresols, and formaldehyde, which are usually employed in approximately equimolecular proportions, although an excess of formaldehyde may also be used.<sup>2</sup> The condensing agents used are almost exclusively substances which form hydroxyl ions, i.e. bases, especially ammonia<sup>3</sup> and salts of alkaline reaction. The reaction is started by heating and first results in the separation of a viscous<sup>4</sup> layer of so-called "liquid resin" of relatively high specific gravity, which may be separated from the aqueous liquid. On carrying the reaction further, the volatile constituents are volatilized and a so-called "solid resin" is obtained, which is liquid whilst hot, but forms in the cold a solid, brittle product of softening point 50–60° C. These two products which are designated liquid and solid "initial products" by Baeckeland,<sup>5</sup> and "resoles" by Lebach,<sup>6</sup> are sold in Germany by the Bakelite G.m.b.H. as "Bakelite A," and form the starting point for the majority of technical applications. In countries other than Germany registered trade names for the analogous

<sup>1</sup> Eibner, *Angew.*, 36, 36 (1293).

<sup>2</sup> On hygienic precautions during the manufacture of these products, see Sachs, *Wiener klin. Wochenschr.*, 34, 356 (1921); *C.* (1921), IV, 853.

<sup>3</sup> German Pats. 228 639; 281,454

<sup>4</sup> On the viscosity of these products, works control, and so forth, see A. A. Drummond, *J. Soc. Chem. Ind.*, 43, 238, 323 (1924); *C.* (1925), I, 366; *Kunstst.*, 15, 3 (1925).

<sup>5</sup> British Pat. 1,921 (1908); U.S. Pat. 942,809 (1909).

<sup>6</sup> *Angew.*, 22, 1598 (1909).

products have also been acquired, such as Redmanol, Sipilite, and so forth, the resole character being indicated by the suffix A, whilst the transformed product is characterized by the suffix C. (See page 146.)

The original method of production just described has been modified in very many directions. The reason for the very intensive attention which has been devoted to the development of the process is, that since it was originally exploited technically by Baekeland, the hardening phenol-formaldehyde resins have found wide technical application and have, consequently, attracted much attention. Apart from numerous proposals which were mainly due to the desire to circumvent the numerous patents by which Baekeland's process was protected, a number of improvements became necessary for the reason that the resoles were also the starting point for the production of resites, phenoplasts, or final products. The first proposals for the technical application of such products, by Smith,<sup>1</sup> Luft,<sup>2</sup> and W. M. Story<sup>3</sup> already aimed at the application of such materials as substitutes for amber, ivory, horn, tortoise-shell, and so forth. As soon, however, as an actually practicable substitute was found by Baekeland, in the form of "Bakelite C," this attracted more attention than the exploitation of the resole resins themselves, which was at that time being technically developed. The requirements which are demanded of a phenoplast, with regard to mechanical properties, colour, fastness to light, capability of being worked, capacity for taking a polish, lustre, and durability, are quite exceptional, and it is not surprising that the development of really satisfactory unfilled products by the processes technically available for the production of resole resins, although solved fundamentally, can only be carried out by the most scrupulous attention to many details.

<sup>1</sup> A. Smith, German Pat. 112,685 (1899); *Chem.-Ztg.* (1900), 740; British Pat. 16,247 (1899); U.S. Pat. 643,012 (1900); Austrian Pat. 3,198.

<sup>2</sup> A. Luft, German Pat. 140,552 (1902); *Chem.-Ztg.* (1903), 374; U.S. Pat. 735,278 (1903); French Pat. 320,991; Austrian Pat. 14,037; British Pat. 10,218 (1902).

<sup>3</sup> German Pat. 173,990 (1905); *C.* (1906), II, 990; British Pat. 8,875 (1905); *Chem.-Ztg. Rep.* (1906), 298; see also French Pat. 353,995 and addition 9,861; Belgian Pat. 210,965 (1908).

The strenuous efforts of the leading firms engaged in this industry and of others, to solve the problem satisfactorily, together with the activities of numerous independent inventors, have given rise to an enormous patent literature.<sup>1</sup> This literature deals with the conduct of the reaction in general, the character, quantity, and application of the condensing agents, the purification of the reaction products, and, finally, with the method of further transformation. Plasticizing agents, fillers, pigments, and so forth, are also dealt with at great length.

It is impossible to divide the processes sharply into those dealing with the production of resoles and of resites respectively; this is obvious, as all resoles should be capable of conversion into resites. In the case of technical materials, which are simultaneously transformed and moulded, after mixing with fillers in the usual manner, the condition of the binding medium which is converted into resite is of essentially the same importance as in the case of plastic masses. In fact, the high electrical insulating properties or resistance to chemical reagents which may be required of such technical products require very special consideration, which may be less necessary in the case of plastic masses. The main variations required deal with the components required for the reaction.

**Raw Materials.** The phenols required for technical phenol-formaldehyde production are mainly phenol itself and the cresols. The higher homologues, polyvalent phenols and naphthols, are usually excluded on account of their higher cost, although used to a limited extent.<sup>2</sup>

Pure phenol, carbolic acid,  $C_6H_5 \cdot OH$ , which is obtained, as are the other phenols, from coal tar, forms a colourless crystalline mass of long needles, of setting point  $39-41^\circ C.$ , and boiling point  $183-184^\circ C.$ , of specific gravity 1.066 at  $150^\circ C.$  It easily acquires a red colour in the air. The product attracts water, has a characteristic odour, and has a strongly caustic

<sup>1</sup> See summary of German Patents, Aladin, *Kunstst.*, 16, 193, 225, 250 (1926); 17, 9, 60 (1927); and of non-German Patents, Aladin, *Kunstst.*, 17, 83, 106, 136, 157, 185, 208, 232 (1927); see also *Kunstst.*, 3, 301 (1913); 4, 268 (1914); 7, 149, 167 (1917); 11, 38 (1924).

<sup>2</sup> See Footnote (11), p. 296.

action on the skin. It can be liquefied by the addition of a small percentage of water and is then very conveniently handled. It is used in the production of phenol-formaldehyde resins, more especially when light-coloured products are required, and particularly as a material for castings which can be hardened. Where light-coloured products are required, it is advisable to distil phenol which may have become red in the air, before use.

The investigation of commercial phenol crystals (*acidum carbolicum*) comprises more especially a determination of the setting point, as this is the best criterion of purity, and is considerably lowered by small amounts of water. Thus, water contents of 0.5, 1, 1.5, and 2 per cent correspond to setting points 38.8° C., 36.9° C., 35.0° C., and 33.2° C. respectively. The phenol must also be soluble to a clear solution in 10 per cent caustic soda solution, and in 15 to 18 parts of water. The colour, odour, and water contents should also be determined. The phenol contents are determined by Koppeschaar's method,<sup>1</sup> or the modified method of Beckurtz,<sup>2</sup> using Seubert's solutions.<sup>3,4</sup> (See page 257.)

Cresols are ordinarily used in the form of so-called technical cresol, which contains the three isomers in proportions which vary considerably, together with varying quantities of homologous phenols, such as xylenols, and impurities such as pyridine bases.

For the preparation of synthetic resins, the two following commercial qualities are mainly used—

100 per cent Liquid Carbolic Acid, Pale (*cresolum crudum*), a clear yellowish to yellow-brown oily liquid, which becomes darker on storage, and

Pure Cresol, a water-clear liquid of boiling point 185–205° C., free from hydrocarbons and containing traces only of phenol and of higher homologues.<sup>5</sup>

<sup>1</sup> *Ztschr. f. analyt. Chem.*, 15, 233 (1876).

<sup>2</sup> *Arch. Pharm.* 24, 561 (1886).

<sup>3</sup> *Idem.*, 18, 321 (1881).

<sup>4</sup> Messinger, Vortmann, *Ber.*, 23, 2753 (1890); also Telle, *J. de Pharm. et de Chim.*, 14, 7, 289 (1901); Bader, *Ztschr. f. analyt. Chem.*, 31, 58 (1892); Toche, *Pharmaz. J.*, 66, 360; Skirrow, *C.* (1918), I, 1198.

<sup>5</sup> On commercial qualities, see Lunge-Berl, *Chem.-techn. Untersuchungen*, Seventh Edition, Berlin (1923), III, pp. 260 *et seq.*

The three isomers always present in commercial cresols have the following physical properties<sup>1</sup>—

	Boiling Point	Softening Point	Specific Gravity at 15° C.
o-Cresol .	190·8° C.	30·5° C.	1·0511
m-Cresol .	202·8° C.	Not below 10·6° C.	1·039
p-Cresol .	201·8° C.	Not below 35° C.	1·039

In testing commercial cresols the first step is a boiling-point determination, during which the main portion should distil between 190° C. and 204° C. Fractions under 190° C. and over 204° C. give an indication of the proportions of phenol and xylenols respectively. Any water contents can be recognized at the commencement of the distillation.

Further tests consist in determination of the solubility in dilute sodium hydroxide solution, any undissolved portion representing hydrocarbons, a test for the presence of sulphur compounds (with copper foil) and an ash determination. The determination of m-cresol is important, as this isomer is exceptionally reactive, as mentioned below, and therefore very valuable for synthetic resin manufacture.

**m-Cresol Determination by Raschig's Method.**<sup>2</sup> If m-cresol is treated with an excess of nitric acid at the boiling point, trinitro-cresol is quantitatively obtained, whilst o- and p-cresol are oxidized to oxalic acid. The determination of m-cresol is effected as follows.

Exactly 10 gm. of the cresol mixture are weighed into a small conical flask and mixed with 15 c.c. ordinary sulphuric acid of 66° Be. The flask is then kept for one hour in a steam-heated drying oven, after which its contents are poured into a wide-necked flask of 1 litre capacity and cooled under the water-tap whilst causing the liquid to swirl round the walls of the flask; the warm, mobile sulphonie acid is thus caused to adhere to the walls of the flask in the form of a thick syrup on cooling.

<sup>1</sup> Boiling Points and specific gravities according to Rosenthaler, *Der Nachweis organischer Verbindungen*, Stuttgart (1914), p. 242; softening points according to Schultz, *Post's Chem.-techn. Analyse*, Third Edition, 11, p. 1079.

<sup>2</sup> *Angew.*, 13, 759 (1900); Lunge-Berl, *loc. cit.*, pp. 260 *et seq.*

The small conical flask in which the cresol was sulphonated, and to which small quantities of sulphonic acid still adhere, is then rinsed with 90 c.c. of ordinary 40 per cent nitric acid, and the whole of this acid is then poured at once into the litre flask, which is immediately vigorously shaken until all the sulphonic acid is dissolved, which requires about 20 seconds. The flask is immediately placed in a draught cupboard, and after the lapse of one minute a vigorous reaction occurs; the contents of the flask boil violently, with evolution of red fumes, after which the liquid suddenly becomes turbid. Oily drops of trinitro-m-cresol separate and collect on the bottom of the flask, and after five minutes have elapsed the reaction appears to be complete; the liquid is, however, allowed to stand for a further five minutes, as a small amount of further nitration occurs; the contents of the flask are then poured into a dish, which already contains 40 c.c. of water, and are rinsed out with a further 40 c.c. of water, which is also added to the contents of the dish. On admixture with the water the oil solidifies, with expansion and evolution of nitrous vapours, forming a crystalline paste of trinitro-m-cresol. This is allowed to stand for at least two hours and is then well crushed with a pestle, poured on to a tared filter, and well drained on the vacuum pump. It is washed with 100 c.c. of water, which is best applied by means of a funnel drawn out to a point, and is finally dried with the filter in a steam drying oven at 95–100° C.

The weight of m-cresol in the sample is found by dividing the weight of trinitro-m-cresol by 1.74.

The method is not applicable to samples containing more than 10 per cent of phenol or much xylenol.<sup>1</sup>

On a method of separating phenol from the three cresols see P. Riehm's baryta method;<sup>2</sup> phenol and o-cresol may be separated from the other cresols by repeated fractionation, after

<sup>1</sup> On other methods, see F. Russig, G. Fortmann, *Angew.*, 14, 157 (1901); J. J. Fox, M. F. Barker, *Chem.-Ztg.*, 44, Rep. 268 (1920); Ditz, Cedivoda, *Angew.*, 12, 873, 897 (1899); Ditz, *idem.*, 13, 1050 (1900); on simultaneous determination of m-cresol and phenol, see W. Qvist, *Ztschr. f. analyt. Chem.*, 68, 257 (1926).

<sup>2</sup> Friedländer, *Fortschritte der Teerfarbenfabrikation*, II (1891), p. 9.

which m- and p-cresol may be separated by Raschig's method,<sup>1</sup> which makes use of the disulphonic acids, or by Rütger's method,<sup>2</sup> according to which p-cresol is separated after esterification with anhydrous oxalic acid.<sup>3</sup> o-Cresol may also be determined with sufficient accuracy in mixtures of cresols.<sup>4</sup>

**Determination of Cresol.** The three isomeric cresols vary very greatly in their behaviour with bromine, according to the conditions of the reaction,<sup>5</sup> so that the Koppeschaar method, which we described when dealing with the termination of phenol, is not directly applicable. According to recent investigations, however,<sup>6</sup> all three cresols may be quantitatively determined by bromination, as has been demonstrated on the most various cresol mixtures by P. W. Danckwörtt and G. Siebler. The time required for bromination depends on the quantity of cresols. With equal quantities, m-cresol is considerably more rapidly brominated quantitatively than the other cresols, requiring a quarter of an hour only, whilst the other two may require 72 hours. In the presence of m-cresol, therefore, special precautions are required. In order to avoid rise of temperature dilute sulphuric acid must be used, and the potassium iodide solution must not be added by opening the stopper, but must be introduced in a small weighing flask before the determination and added at the right moment by inverting this. For bromination over a prolonged period it is necessary to prolong the neck of the flask above the ground joint of the stopper, in order that any escaping bromine may be absorbed by potassium iodide solution added above the stopper. When titrating o-cresol, a blue coloration occurs half an hour after the completion of the titration, and must be taken into account. With cresol contents of 0.6 to 0.7 gm. per litre, quantitative

<sup>1</sup> German Pats. 112,545, 114,975; *Jahresber. d. Pharm.*, 35, 271 (1900).

<sup>2</sup> *Jahresber. d. Pharm.*, 38, 264 (1903).

<sup>3</sup> See also German Pat. 232,071.

<sup>4</sup> E.g. H. M. Dawson and C. A. Mountfort, *Journ. Chem. Soc.*, London, 113, 923, 935 (1918); *C.* (1919), 1, 929; 11, 818; by the melting-point diagram or viscosimetrically, according to J. Scheiber and S. Werndt (unpublished method).

<sup>5</sup> Vaubel, *Journ. f. prakt. Chem.* (2) 48, 74 (1893); Ditz, Cediwoda, *Angew.*, 12, 873, 897 (1899).

<sup>6</sup> P. W. Danckwörtt, G. Siebler, *Arch. Pharm.*, 264, 439 (1926); *C.* (1926), 11, 2618; Ulrich, Kather, *Angew.*, 39, 229 (1926).



results are obtained after standing for 24 hours. The procedure in the case of *m*-cresol is as follows.

The weighing bottle in the conical flask with ground-glass stopper is charged with 10 c.c. of 20 per cent potassium iodide solution. The following are then added in sequence: 30 c.c. of *N*/10 potassium bromate solution (2.7837 gm.

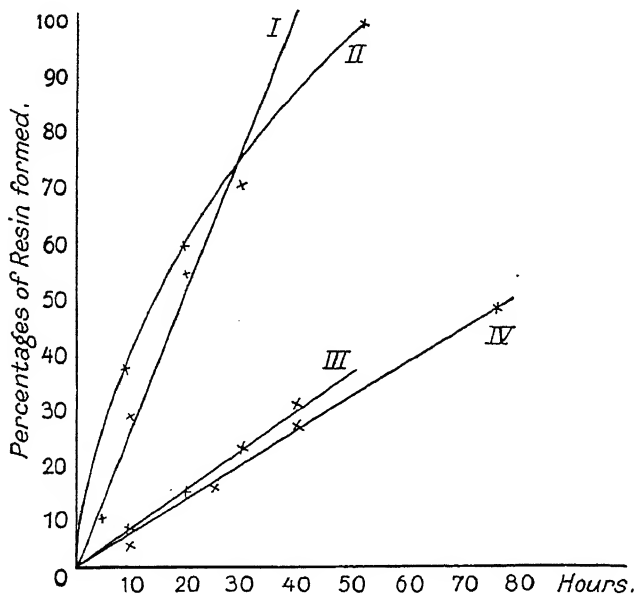


FIG. 5. REACTION BETWEEN PHENOLS AND FORMALDEHYDE

per litre), 25 c.c. of the *m*-cresol solution under investigation and 30 c.c. of dilute sulphuric acid (1.5), these solutions being poured down the wall of the flask and well mixed. Finally, 10 c.c. of 20 per cent potassium bromide solution must be added as quickly as possible. The contents of the weighing bottle and of the flask must, of course, be kept quite separate. After a quarter of an hour (or after the necessary longer period in the case of the isomeric cresols) the weighing bottle is inverted, the whole well mixed, and the iodine titrated after five minutes.

The individual isomers, o-, m-, and p-cresol, react with varying facility with formaldehyde, and yield products of differing character. Thus, m-cresol reacts with five times the velocity of o- and p-cresol.<sup>1</sup> The resin obtained from m-cresol and formaldehyde is exceptionally hard and resistant after transformation. The relatively very high velocity of resin-formation of m-cresol is shown by the diagram (Fig. 5), which shows the reaction curves of pure m-cresol, a commercial cresol, a mixture of pure cresols in the same proportions as in technical cresol (40 per cent m-cresol, 30 per cent p-cresol, and 30 per cent o-cresol), and of pure phenol, in each case with the equimolecular proportion of formaldehyde, the same experimental conditions being carefully maintained in all the experiments, which were conducted in the absence of condensing agents. The accelerating action of the impurities in the technical products is very noticeable. The curvature of the curve for technical cresol, as compared with the rectilinear course of the curves for the pure products, is also especially noteworthy.<sup>2</sup>

The high reaction velocity of m-cresol makes it necessary to take special account of the proportion of this substance when using technical cresols. It has also been the cause of the development of special processes.

Thus, formaldehyde resins are alleged to be obtained from m-cresol and its higher homologues,<sup>3</sup> such as m-xylenol, which are distinguished by pale colour, hardness, and freedom from odour. The high reaction velocity of m-cresol even enables the use of condensing agents to be dispensed with, so that

<sup>1</sup> German Pat. 301,374 (1913); *C.* (1919), IV, 918; see also German Pat. 304,384.

<sup>2</sup> These curves embody the authors' own experiments. They used pure phenols (Kahlbaum) and purified 25-10% formaldehyde solution. A uniform addition of alcohol was also made in order to obtain more homogeneous conditions. The reaction mixture was introduced into a steamed Jena glass flask heated under reflux in a water bath, the height of water in which was automatically maintained at a constant level and which was also permanently maintained at the boil. Equal quantities were removed at regular intervals by a pipette, after which the free phenols were removed by steam distillation, which was always carried out for the same length of time in the same apparatus. The residual resin was determined by evaporation, short drying for the same time and temperature in the drying oven, and weighing.

<sup>3</sup> *Chem. Fabr.*, K. Albert and L. Berend, German Pat. 301,374 (1913); *C.* (1919), IV, 918; *Kunstst.*, 10, 33 (1920).

resins may be obtained which are especially suitable for electrotechnical purposes in consequence of neutrality in the hardened condition. As, however, the use of pure m-cresol as a raw material would be far too expensive, the above process has been altered accordingly.<sup>1</sup> Thus, technical cresol mixtures are employed, containing 50 to 60 per cent of m-cresol, which have previously been freed from o-cresol in a suitable manner. These are then treated with formaldehyde for such a period and in such a manner that, as far as possible, the m-substituted phenols are alone caused to react, after which the remaining phenols and so forth are removed, for example, by distillation in vacuo. Although it is scarcely possible to obtain pure meta-cresol resins in this manner, they contain these in a much more concentrated form. In this process m-substituted xylenols have also proved to be utilizable.

Baekeland also produced a resin from m-cresol and formaldehyde<sup>2</sup> in the presence of both acid or basic condensing agents. He also investigated closely the conditions under which o- and p-cresol yielded hardening resins. Generally speaking, both cresols, but especially the o-compound, showed a strong tendency to form fusible and soluble resins of the saliretine (Novolak) type. In the presence of sufficient quantities of formaldehyde, hardening resins may be obtained, but require somewhat prolonged heating for hardening. Baekeland also called attention to certain advantages which arise through the presence of such constituents, which harden less readily, in phenol-formaldehyde resins; they produce a form of plasticizing effect on the hardened product.<sup>3</sup> Thus, the formaldehyde resins obtained from technical cresol are fairly brittle in the soluble form, but become astonishingly elastic on hardening. Consequently, billiard balls produced from such material may be thrown on to a stone floor without injury and rebound as though made of rubber. This property is ascribed to the

<sup>1</sup> *Chem. Fabr.*, K. Albert and L. Berend, German Pat. 304,384 (1913); *C.* (1919), IV, 1053; Berend, U.S. Pat. 1,214,414 (1917); *Kunstst.*, 7, 178 (1917).

<sup>2</sup> U.S. Pats. 1,088,677-8 (1914).

<sup>3</sup> U.S. Pats. 1,306,681 (1919); 1,401,953 (1922); *C.* (1923), II, 1000.

colloidal character of the products, on the assumption that portions of this act as a dispersive medium and the remainder as a skeletal gel.

Phenolic products other than phenol and the cresols play but an unimportant part in the production of synthetic resins. We have already referred to the utilizability of *m*-substituted xylenols, but pure xyleneol-formaldehyde resins are only utilisable under special conditions, as they are only slightly soluble in alcohol, without any compensating greater solubility in benzene, for example. They are, however, not undesirable as components of the ordinary phenol-formaldehyde resins. It should be noted that cresol resins containing more than 20 per cent of xyleneol resins form heavy precipitates on treatment with alcohol, which only gradually disappear.

Among other phenolic components the naphthols must be mentioned, although the high price of these excludes their utilization in practice in most cases. Naphthol-formaldehyde resins are generally distinguished by high melting point, and show the special peculiarity that on heating to above 200° C. they are stated to become insoluble in alcohol, but soluble in benzene and in oil.<sup>1</sup> The melting process is associated with dark coloration.

Apart from the phenols already referred to, attempts have been made to utilize for resin formation with formaldehyde the more or less crude fractions of various tars, in order thus to separate these substances in an economic manner and avoid the necessity for separating them specially. Thus, a resin which is easily soluble in alcohol and acetone, but soluble with difficulty in benzene, ether, and chloroform, is obtained by the action of formaldehyde on tar oils of boiling point about 180–230° C., and subsequent distillation of the unchanged substances which accompany the phenols.<sup>2</sup> Also the soap solution obtained with concentrated caustic alkali solution and wood-tar gives with formaldehyde a hard, brown resin, soluble

<sup>1</sup> P. Esholz and J. Altendorf, German Pat. application E. 23,046, Class 22h (25th March, 1918). If true, such a process could naturally be applicable to Novolak products only.

<sup>2</sup> Gesellschaft für Teerverwertung m.b.H., German Pat. application G., 46,140, 22h (21st January, 1918).

in solvent naphtha.<sup>1</sup> Lingner<sup>2</sup> had already obtained a similar condensation product. These last resins possess peculiar properties in consequence of the creosote contents of wood-tar.

Phenol-formaldehyde products of the usual type have been obtained from fractions of low temperature tar,<sup>3</sup> by which means a separation from the accompanying hydrocarbons could be effected, as these were easily removed after the resinification of the phenols with formaldehyde or other aldehydes. Crude tar was used, from which the highly viscous substances had been removed; the fractions mainly used were those boiling from 150–250° C., and between 250–300° C. Ammonia and benzylamine were used as catalysts. According to the proportions of phenols and formaldehyde solution used, soluble and fusible or hardening resins could be obtained; it was found, however, that with benzylamine as condensing agent, hardening resins could not be obtained from the higher fractions, more especially from that boiling from 260–300° C.<sup>4</sup>

The use of a number of other phenols and their derivatives has been recommended.<sup>5</sup> The primary products of the interaction

<sup>1</sup> Chem. Fabr., Flörsheim, H. Noerdlinger, German Pat. 338,854 (1919); *Frdl.*, XIII, 658; *C.* (1921), IV, 714.

<sup>2</sup> French Pat. 329,971 (1903); German Pat. 161,939; *C.* (1905), II, 863.

<sup>3</sup> Glud, Breuer, *Ges. Abhandlungen zur Kenntnis der Kohle*, 4, 221 (1919-1920); *C.* (1921), II, 855.

<sup>4</sup> See also Anderson, Maclaurin, British Pat. 183,629 (1921); *C.* (1923), IV, 669; *Kunstst.*, 13, 125 (1923); the resins are soluble in benzene; also Terwilliger, British Pats. 218,277, 218,638; French Pat. 583,582 (1924); *C.* (1926), II, 1474; F. v. Briesen, U.S. Pats. 1,624,082, 1,624,638; *C.* (1926), II, 1474; (1928), I, 978 (Utilization of coal-tar oils, formaldehyde, and ketones); *Kunstst.*, 16, 254 (1926); Comp. des Mines de Vicoigne, Nocux et Drocourt, French Pat. 607,655 (1925); *C.* (1926), II, 2234, phenolic tar-oils or low temperature tar-oils with formaldehyde; see also A. Nowak A.-G., U.S. Pat. 1,658,281; *C.* (1928), II, 816; American Cyanamid Co., U.S. Pat. 1,669,674; *C.* (1928), II, 1393.

<sup>5</sup> Polyvalent Phenols; Labbe, French Pat. 468,879 (1913); *Kunstst.*, 5, 201 (1915); L. Helm, French Pat. 602,704 (1924); *C.* (1926), II, 1476; *Kunstst.*, 16, 255 (1926); Mixtures of polyvalent phenols with phenol: Dubrisay, French Pat. 556,153; *C.* (1923), IV, 832; *Kunstst.*, 13, 125 (1923); Resorcin: Peter, U.S. Pat. 1,147,264; H. Burneister, British Pat. 275,678 ("Burmin"); see, however, W. H. Story, German Pat. 173,990; Pyrogallol: McCoy, U.S. Pat. 1,286,372 (1918); Eugenol: Andresen, British Pat. 110,154 (1917), for stopping teeth; Chlorphenols: Steinmetz, U.S. Pat. 1,215,072 (1917); *Kunstst.*, 7, 237 (1917); Cyclohexanol: C. Ellis, U.S. Pat. 1,557,521 (1923); *C.* (1926), I, 1723; *Kunstst.*, 16, 116 (1926); Tetrahydronaphthols: Aktiengesellschaft für Anilin-Fabrikation, German Pats. 346,434 (1918); 356,223 (1918), *Frdl.*, XIII, 655, 1118; resins soluble in alcohol, benzene, turpentine oil, and linseed oil, French Pat. 518,553; British Pat. 165,322 (1920); *C.* (1921), IV, 471, 1014.

between aldehydes or ketones and phenols are also often used as raw materials for resin-forming condensation with formaldehyde, and so forth. This is especially the case for phenol-alcohols and methylene-diphenol products of all kinds.<sup>1</sup>

*Formaldehyde*,  $\text{H} \cdot \text{CHO}$ , is a gas of sharp smell, obtainable commercially in the form of aqueous solutions under the name of formol or formalin; these solutions contain 30 per cent or 40 per cent by weight (or about 36.5 per cent by volume), and have specific gravity 1.08. These solutions usually contain very small quantities (up to 0.2 per cent) of formic acid, and considerable quantities of methyl alcohol, especially in the 40 per cent form. Formaldehyde is also used in its polymerized forms, as trioxymethylene, polyoxymethylenes and paraformaldehyde, and also in the form of its ammonia compound, hexamethylenetetramine,  $\text{C}_6\text{H}_{12}\text{N}_4$ . Formaldehyde is manufactured by the oxidation of methyl alcohol.<sup>2</sup> Other methods of manufacture are still being developed.<sup>3</sup>

In aqueous formaldehyde solutions, which are sharp smelling liquids, the compound is present in both the monomolecular and polymeric forms, and as hydrated products of both of these. A condition of equilibrium exists between these various substances, which is dependent on the temperature and concentration, and is of such a character that increase of concentration and decrease of temperature both favour the formation of polymers.

The boiling point of pure formaldehyde solutions is between 99° and 100° C. It is lowered by the presence of methyl alcohol, which can be detected in that way, and which is added to commercial qualities to the extent of 10 to 18 per cent to prevent the separation of paraldehyde. On distillation, the distillate obtained is always poorer in formaldehyde than the

<sup>1</sup> E.g. Bakelite Corp., U.S. Pat. 1,637,512; French Pat. 634,925; Beatty, U.S. Pats. 1,113,926, 1,158,962, 1,225,748-49-50; C. Kulas, C. Pauling, German Pat. 431,619.

<sup>2</sup> On the literature, see *B. ilst.*, 1, 558, 560.

<sup>3</sup> On the catalytic production from carbon monoxide and hydrogen, see B. Neumann and P. Biljevic, *Angew.*, 40, 1469 (1927); on production by the catalytic oxidation of acetaldehyde, see Consortium f. elektrochem. Ind., Brit. Pat. 178,842 (1922).

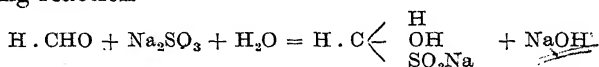
residue. At 18° C. the specific gravities of pure aqueous formaldehyde solutions are as follows—<sup>1</sup>

Gm. CH <sub>2</sub> O per 100 c.c.	Gm. CH <sub>2</sub> O per 100 gm.	Sp. gr. d <sub>4</sub> <sup>18</sup>
2.24	2.23	1.0054
4.66	4.60	1.0126
11.08	10.74	1.0311
14.15	13.59	1.0410
19.89	18.82	1.0568
25.44	23.73	1.0719
30.17	27.80	1.0853
37.72	34.11	1.1057
41.87	37.53	1.1158

Aqueous formaldehyde solutions are miscible with alcohol in all proportions, but not with ether.

They are tested for acid contents, evaporation residue and the presence of heavy metals, such as copper and iron, which might cause discoloration of the resins. The German Pharmacopeia stipulates that aqueous formaldehyde solutions (1:4) shall not be changed by the addition of silver nitrate or barium nitrate solutions, or of sulphuretted hydrogen solution. The ignited residue from 20 c.c. of formaldehyde solution is not to exceed 2 mg. The determination of the formaldehyde contents is important and can be effected by various methods.<sup>2</sup>

**Sodium Sulphite Method.**<sup>3</sup> The method depends on the following reaction—



The German Pharmacopeia gives the following directions—

At least 37.8 c.c. of N. HCl must be required for the complete decolorization of a mixture of 3 c.c. formaldehyde

<sup>1</sup> Auerbach, *Arbeiten aus dem kais. Gesundheitsamte*, 22, 578; see Beilst., Fourth Edition, p. 561, where literature references on the various details will be found.

<sup>2</sup> Lunge-Berl, *Chem. techn. Untersuchungsmethoden*, Seventh Edition, Berlin (1923), III, p. 1146 *et seq.*, whence some of the above instructions have been taken.

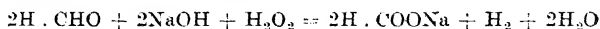
<sup>3</sup> Lemme, *Chem.-Ztg.*, 27, 896 (1903); compare also Auerbach, *Arbeiten aus dem kais. Gesundheitsamte* 22, 588 (1905); Doby, *Angew.*, 20, 355 (1907); Lockemann, Croner, *Ztschr. f. analyt. Chem.*, 54, 23 (1915); Feinberg, *Am. Chem. J.*, 49, 87 (1905); *Ztschr. f. analyt. Chem.*, 54, 231 (1915).

## PHENOL-ALDEHYDE RESINS

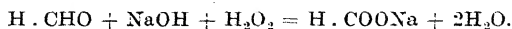
solution, 50 c.c. of a freshly-prepared sodium sulphite solution (containing 25 gm. of crystallized sodium sulphite per 100 c.c.), and 1 drop of phenol-phthalein solution, after deduction of the quantity of N . HCl required to decolorize 12 c.c. of sodium sulphite solution, 80 c.c. of water and 1 drop of phenol-phthalein solution alone. Such 37.8 c.c. of N . HCl correspond to a formaldehyde content of 35 per cent; 1 c.c. N . HCl corresponds 0.03002 gm. of formaldehyde.

**Blank and Finkenbeiner's Method.**<sup>1</sup> (a) W. FRESSENIUS AND L. GRUNHUT'S MODIFICATION.<sup>2</sup> About 3 gm. of formaldehyde weighed into a small cylindrical weighing bottle with ground-glass stopper. Into a conical flask of 500 c.c. capacity, 25 to 30 c.c. of 2N . NaOH, free from carbonate, are now introduced, and the opened weighing bottle is then cautiously slipped in in such a manner that none of its contents are spilt, and that it stands erect on the bottom of the flask. The liquids are then mixed by swinging the flask and the addition of 50 c.c. of 3 per cent hydrogen peroxide immediately commenced, which is added from a dropping funnel at such a rate that the whole quantity is introduced in three minutes. The mixture is then allowed to stand for two or three minutes, or for ten minutes in the case of material containing less than 30 volumes per cent of formaldehyde, the funnel and walls of the flask then rinsed with water free from carbon dioxide and the excess of alkali titrated back with N . H<sub>2</sub>SO<sub>4</sub>, using good litmus solution as an indicator. Any acidity of the formaldehyde or of the hydrogen peroxide which is used, must be determined with N/10 . NaOH and allowed for.

1 c.c. of N . NaOH corresponds to 0.03002 gm. formaldehyde, in accordance with the equations—



and



(b) MODIFICATION OF HEYWOOD AND SMITH.<sup>3</sup> 3 c.c. of formalin solution are mixed with 50 c.c. N . NaOH in a 300 c.c.

<sup>1</sup> *Ber.*, 31, 2979 (1898); 32, 2141 (1899).

<sup>2</sup> *Ztschr. f. analyt. Chem.*, 44, 13 (1905).

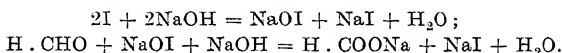
<sup>3</sup> *J. Am. Chem. Soc.*, 27, 1183 (1905); *Angew.*, 20, 79 (1907).



conical flask. A small funnel is then inserted in the neck of the flask, and 50 c.c. of 3 per cent hydrogen peroxide solution are added. The flask is then heated for five minutes on the water-bath, shaking occasionally. After cooling, the excess of caustic alkali is titrated with N.  $\text{H}_2\text{SO}_4$ . A blank experiment is carried out in the same manner, and the difference of the two titrations is used to calculate the result. (See above.) Either litmus or phenol-phthalein may be used as an indicator, it being only necessary to use the same indicator for both the actual and the blank titrations.<sup>1</sup>

**G. Romijn's Iodometric Process.**<sup>2</sup> MODIFICATION OF THE VEREIN FÜR CHEMISCHE INDUSTRIE<sup>3</sup> AND OF FRESENIUS AND GRUNHUT.<sup>4</sup> 25 gm. or 25 c.c. are weighed into a tared weighing bottle with ground stopper and then quantitatively rinsed into a 500 c.c. measuring flask in which they are diluted to 500 c.c. 5 c.c. of this solution are introduced into a flask with a well-fitting ground-glass stopper and 30 c.c. of N. NaOH added, which are measured with sufficient accuracy in a measuring cylinder. About 50 c.c. of N/5 I solution are immediately added from a burette, with constant shaking, until the liquid is bright yellow in colour. The flask is then closed, shaken for a further half minute, acidified with 40 c.c. N.  $\text{H}_2\text{SO}_4$  (which may be measured in a measuring cylinder), and after stoppering and allowing to stand for a short time the iodine is titrated back with N/10 thiosulphate solution.

1 c.c. of N/5 I solution corresponds to 0.003002 gm. formaldehyde, in accordance with the equations—



We must refer to the literature regarding other methods of determining formaldehyde,<sup>5</sup> and the determination of methyl alcohol.<sup>6</sup>

<sup>1</sup> See also Robin, *Angew.*, 21, 1752 (1908); *Ref. n. Ann. de Chim. analyt. appl.* 13, 53 (1908); Schoorl, *Pharm. Weekbl.*, 43, 1155; *C.* (1906), II, 1873.

<sup>2</sup> *Ztschr. f. analyt. Chem.*, 36, 18 (1897).

<sup>3</sup> *Idem.*, 39, 60 (1900).

<sup>4</sup> *Idem.*, 44, 20 (1905).

<sup>5</sup> See also Lunge-Berl, *loc. cit.*, p. 1151 *et seq.*

<sup>6</sup> See also Lockemann, Croner, *Ztschr. f. analyt. Chem.*, 54, 15 (1915).

The only difference in practical application between the two ordinary commercial qualities of formaldehyde solution, namely, 30 and 40 per cent (see page 297), appears to be that with the stronger product the reaction proceeds more intensively, which is possibly not due to the concentration alone, but also to the homogenizing action of the methyl alcohol which is present in substantial amount in the 40 per cent solution.

While the aqueous solutions of formaldehyde above referred to are used for most technical processes, F. Pollak also used more concentrated solutions, or a polymerized trioxymethylene.<sup>1</sup> It was found that when the polymeric product was employed the condensation occurred in the presence of extremely small amounts of acids or bases, or even without any condensing agent within a reasonable time. After thorough washing with water, the resins obtained are distinguished by exceptionally pale colour and by fastness to light, which is ascribed to the avoidance of the formation of leuco-compounds, especially of the triphenylmethane series, which is favoured by the presence of condensing agents, and to the removal of excess of phenol and of similar dyestuff producing substances by washing.

A considerable number of polymers of formaldehyde have been identified, more especially by F. Auerbach and Barschall.<sup>2</sup> These are produced either on evaporation of the aqueous solutions (paraformaldehyde), or by the action on them of sulphuric acid. They differ widely in their physical and chemical properties. They have recently been studied in detail by H. Staudinger and his pupils, who found that the following simple explanation could be given for the differences between  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and

<sup>1</sup> German Pat. 263,109 (1909); *C.* (1913), II, 834; *Kunstst.*, 3, 357 (1913); German Pat. 310,894 (1911); *C.* (1919), II, 428; *Frdl.*, XIII, 643; *Kunstst.*, 9, 136 (1919); German Pat. 388,766 (1911); *C.* (1924), II, 1281; *Frdl.*, XIV, 1144; German Pat. 394,253 (1919); *Frdl.*, XIV, 1146; *C.* (1924), II, 1028; *Kunstst.*, 15, 122 (1925); U.S. Pat. 1,210,982; *Kunstst.*, 7, 162 (1917); U.S. Pat. 1,211,227 (1917); *Kunstst.*, 7, 141 (1917); U.S. Pat. 1,369,352 (1921); *C.* (1921), IV, 809; British Pat. 1343 (1912); *Kunstst.*, 3, 395 (1913); British Pats. 18,281 (1912); 20,977 (1914); 14,490 (1915); Austrian Pat. 96,660 (1912); *C.* (1924), II, 1282; Swiss Pat. 73,579 (1916); Hungarian Pat. 41,636; Dutch Pat. 1859; *Kunstst.*, 8, 273 (1918); Swedish Pat. 53,240; *C.* (1923), IV, 730; French Pats. 420,404; 447,969.

<sup>2</sup> *C.* (1905) II, 1082.

$\delta$ -polyoxymethylenes.<sup>1</sup> Commercial paraformaldehyde is a poly-oxymethylene hydrate, as is also  $\alpha$ -polyoxymethylene; the two differ from one another by the degree of polymerization;  $\alpha$ -polyoxymethylene contains much less water and contains many more simple formaldehyde molecules in polymerized form. The  $\beta$ -polyoxymethylene, which is obtained from concentrated formaldehyde solutions by precipitating with a large amount of strong sulphuric acid, is a sulphuric acid ester of this polyoxymethylene hydrate, and the peculiar properties of this modification are to be ascribed to this combined sulphuric acid.<sup>2</sup> The  $\delta$ -polyoxymethylene, which can only be produced in the presence of methyl alcohol, must be regarded as a polyoxymethylene-dimethylether. It is thus a final member, containing a maximum of formaldehyde, of the series of methyl ethers there described.<sup>3</sup> The low reactivity of this last modification is due to the replacement of the hydroxyl group by the ether group; it is, of course, well known that in the case of simpler compounds also, the ethers are more stable than the corresponding alcohols. Finally, in the formation of  $\delta$ -polyoxymethylene, which is produced by prolonged treatment of the  $\gamma$ -modification with boiling water, the easily attacked C—O—C—O grouping has been transformed into the O—C—C—O grouping at various positions of the large molecule; for it has been found that by fission of this substance glyoxalic derivatives are formed, and the special properties of this modification, such as its low volatility, are thus explained." Regarding the formulae, see page 61.

The use of formaldehyde gas has also been proposed for the production of phenol-formaldehyde resins.<sup>4</sup>

Hexamethylene-tetramine,  $C_6H_{12}N_4$ , may also be used in place of the various formaldehyde products.<sup>5</sup> This crystalline

<sup>1</sup> Staudinger, *Ber.*, 59, 3024 (1926).

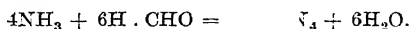
<sup>2</sup> This fact may also have some bearing on Pollak's method of producing phenol-formaldehyde resins.

<sup>3</sup> Staudinger, *Ber.*, 59, 3024 (1926).

<sup>4</sup> Aylsworth, U.S. Pat. 1,029,737 (1912); *Kunstst.*, 3, 114, 177 (1913); French Pat. 441,017; British Pat. 3498 (1911); see also Story, British Pat. 8875 (1905); Progress Akt.-Ges., German Pat. 426,866 (1923); *C.* (1926), II, 1206.

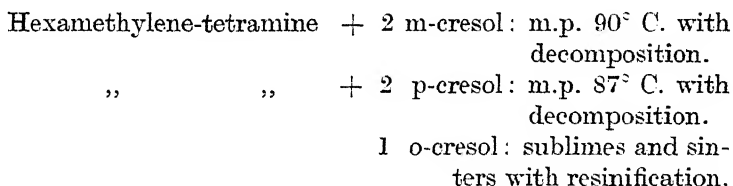
<sup>5</sup> On the synthetic resins so produced, see *Kunstst.*, 5, 116, 275 (1915).

material is produced on mixing formaldehyde and ammonia, water being eliminated with considerable evolution of heat, according to the equation—



The hexamethylene-tetramine thus produced forms addition products with phenols, which are at once obtained if the components are brought together in solution in a suitable solvent, preferably in molecular proportions. Thus, on mixing aqueous solutions of hexamethylene-tetramine and phenol, the molecular compound of 1 mol. of the former with 3 mol. of the latter separates in crystalline form. It melts and decomposes at 115–124° C.<sup>1</sup> On evaporating alcoholic solutions of hexamethylene-tetramine and phenol, a molecular compound of 1 mol. of each substance is formed, which melts at 158–159° C. with resinification.<sup>2</sup>

Molecular compounds with hexamethylene-tetramine can be similarly produced with many other phenols, as instanced by the following obtained from cresols<sup>3</sup>—



The decomposition which occurs on melting is characteristic of such addition-compounds, and is accompanied by liberation of ammonia and of a gas, the smell of which resembles that of methylamine, together with the formation of resins which are insoluble and infusible.<sup>4</sup> This reaction has been applied to the production of hardening phenol-formaldehyde resins. It was found that by employing more phenol for this purpose than

<sup>1</sup> Tollens, Moschatos, *Ann.*, 272, 271 (1893).

<sup>2</sup> Scheiber, Sändig, *Dissert.* Sändig, Leipzig (1923)

<sup>3</sup> Harvey, Bäckeland, *J. Ind. Eng. Chem.*, 13, 135 (1921); *C.* (1921), IV, 1014.

<sup>4</sup> Lebach, *Angew.*, 22, 1600 (1909); Knoll & Co., Belgian Pat. 204,811 (1907); Wetter (Knoll & Co.), British Pat. 28,009 (1907).

corresponded to the proportion present in hexamethylene-tetramine-triphenol, namely, 6 mol. phenol to 7 methylene groups, decomposition occurs with production of ammonia only.<sup>1</sup> The ammonia which is liberated is conveniently led into formaldehyde solution in order to produce a further quantity of hexamethylene tetramine.

The proportion between the quantities of hexamethylene-tetramine and phenol used is, therefore, the factor which decides the character of the resin which is produced. Thus, on heating 12 or more molecules phenol with 1 mol. hexamethylene-tetramine a soluble, permanently fusible product is obtained, resembling Novolak. The less the proportion of phenol used, the more easily are hardening resins obtained, and with a proportion of 5 mol. phenol to 1 mol. hexamethylene-tetramine, the end product of the heating operation is a substance which remains hard at all temperatures and is no longer capable of becoming soft or plastic. The reaction may, of course, be interrupted at an earlier stage, so that a product is obtained which is still capable of being hardened.

Condensation can be effected by heating the mixture of the two components,<sup>2,3</sup> whereby the temperature may not exceed a certain point, corresponding to the hardening temperature of the product produced. Heating is frequently effected under pressure.<sup>4</sup> The presence of a solvent such as xylene,<sup>5</sup> alcohol or acetone<sup>6</sup> has been found advantageous for controlling the

<sup>1</sup> Redman, Weith, Brock, *J. Ind. Eng. Chem.*, **6**, 3 (1914).

<sup>2</sup> B. B. Goldsmith, U.S. Pat. 1,230,829 (1917); British Pat. 6,363 (1912).

<sup>3</sup> On a charge consisting of addition compounds of hexamethylene-tetramine with phenols and phenol-alcohols, see Bakelite Cor. and Baeland. U.S. Pat. 1,442,420 (1919); *C.* (1926), II, 1468; *Kunstst.*, **16**, 253 (1926); on the admixture of an intermediate product from phenols and hexamethylene-tetramine with another from phenol and anhydrous polymeric formaldehyde, see W. O. Snelling, U.S. Pat. 1,462,771 (1920); *C.* (1926), II, 1469; *Kunstst.*, **16**, 254 (1916); on the utilization of a salt of hexamethylene-tetramine (the chloride) for resinification with phenols, see Baeland, Thurlow, U.S. Pat. 1,187,231 (1916); *Kunstst.*, **6**, 298 (1916); on the use of anisol, phenylmethylketone, etc., for interaction with hexamethylene-tetramine, see Wade, Karpen, British Pat. 9,292 (1914); Redman, U.S. Pat. 1,209,333 (1916); *Kunstst.*, **7**, 115, 162 (1917); **8**, 10 (1918); on an addition product between anisol and hexamethylene-tetramine, see J. Scheiber and K. Sändig, *Dissert.* Sändig, Leipzig (1923).

<sup>4</sup> Redman, Weith, Brock, U.S. Pat. 1,368,753 (1918); *C.* (1921), II, 743.

<sup>5</sup> Goldsmith, U.S. Pat. 1,375,959 (1921); *C.* (1922), II, 580.

<sup>6</sup> Redman, U.S. Pat. 1,107,703 (1914); *Kunstst.*, **5**, 177 (1915).

reaction. Water may also be used. The reaction commences at 60–80° C. with rapid evolution of ammonia. According to the proportions of the components the temperature must then either be kept down by cooling, in which case the duration of the reaction may amount to several hours, or it may be raised to 140–180° C., at least if products of the type of Novolak are required.

In the production of hardening products it is found to be advantageous first to produce a soluble and permanently fusible resin, from 11 mol. cresol and 1 mol. of hexamethylene-tetramine, and then to harden by the further addition of formaldehyde or hexamethylene-tetramine.<sup>1</sup> This illustrates the true practical importance of hexamethylene-tetramine, for as recovered from aqueous solution<sup>2</sup> this product is far too costly to be used for the production of hardening resins. It might have a certain importance for the production of amber substitutes only,<sup>3</sup> in which the question of cost is not of predominant importance.

Otherwise, hexamethylene-tetramine can only be advantageously used for improving the hardening properties of certain products which would otherwise be incapable or only slightly capable of being hardened.<sup>4</sup> This question will be further dealt with when describing hardening processes. (Pages 326 *et seq.*)

A number of other substances have been recommended as suitable formaldehyde substitutes for interaction with phenols in order to produce resins of the phenol-formaldehyde type. Among these are methylene chloride<sup>5</sup> (see also page 207).

<sup>1</sup> Redman, U.S. Pat. 1,188,014 (1916); *Kunstst.*, 6, 282–3 (1916); U.S. Pats. 1,242,592–3 (1917); *Kunstst.*, 8, 143 (1918); British Pats. 119,252–3; *Kunstst.*, 10, 101 (1920).

<sup>2</sup> On the use of a mixture of hexamethylene-tetramine and  $\text{NH}_4\text{Cl}$  produced by the action of  $\text{NH}_3$  on  $\text{CH}_2\text{Cl}_2$ , see S. Karpen & Bros., C. B. Carter, U.S. Pat. 1,566,823 (1924); *C.* (1916), I, 2854; H. Wate, British Pat. 255,692 (1925); see also U.S. Pat. 1,543,369 (1922); Canadian Pats. 220,985, 234,506 (1923); British Pat. 220,985 (1923); French Pat. 566,854 (1923); *C.* (1926), II, 1471; *Kunstst.*, 16, 254 (1926).

<sup>3</sup> Baekeland, U.S. Pat. 1,187,230 (1916); *Kunstst.*, 6, 282, 297 (1916).

<sup>4</sup> Baekeland, *J. Ind. Eng. Chem.*, 1, 159 (1909).

<sup>5</sup> See also Holzverkohlungsindustrie A.G., British Pat. 196,265; *C.* (1923), IV, 730; *Kunstst.*, 13, 125 (1923); 14, 42 (1924).

thioformaldehyde,<sup>1</sup> methylal,<sup>2</sup> anhydroformaldehyde-aniline,<sup>3</sup> formal glycerine,<sup>4</sup> and so forth, or, in more general terms, the cyclic ethers of polyvalent aliphatic alcohols with an aldehyde (for example from formaldehyde and glycerine),<sup>5</sup> concentrated solutions or loose compounds of polymerized formaldehyde with phenols,<sup>6</sup> a reaction product of carbon monoxide, hydrogen, and ammonia,<sup>7</sup> and so forth.<sup>8</sup>

**Proportions of the Components.** As will be gathered from the preceding description, the proportion between the components, i.e. the weight of phenol used per unit weight of formaldehyde, is the predominant factor in the formation of hardening resins. It may be assumed that when the condensation is carried to practical completion approximately equimolecular proportions are required in order to produce normal hardening phenol-formaldehyde resins, such as are more particularly suitable for use as binding agents. For special products only, such as for materials suitable for casting (which are employed for the manufacture of amber and ivory substitutes, and so forth), a higher proportion of formaldehyde is usually introduced into the reaction mixture, in order to promote the combination of still higher quantities of formaldehyde. In this way alone is the exceptional elasticity produced which characterizes the hardened products finally obtained. An excess of formaldehyde also hinders the formation of coloured compounds.<sup>9</sup> An excess of formaldehyde is also frequently employed in order to enable a further condensation with urea, aniline, or some other

<sup>1</sup> G. Brunn, Austrian Pat. 100,564 (1921); *C.* (1926), II, 1477; *Kunstst.*, 16, 231 (1926).

<sup>2</sup> See S. Karpen & Bros., C. B. Carter, A. E. Cox, U.S. Pat. 1,566,817 (1922); British Pat. 254,703; British Pat. 605,736 (1925); *C.* (1926), II, 1471; U.S. Pat. 1,645,226; *C.* (1928), II, 814.

<sup>3</sup> B. B. Goldsmith, U.S. Pat. 1,168,626; 1,188,439, 1,228,428; *Kunstst.* 6, 174, 282 (1916); 7, 323 (1917); 9, 137 (1919); Baekeland, U.S. Pat. 1,216,265 (1917); W. Achtmeyer, U.S. Pat. 1,429,267 (Afterwards hardened with para-formaldehyde); Canadian Pat. 237,679.

<sup>4</sup> Carboloid Products Cor., U.S. Pat. 1,523,459.

<sup>5</sup> Les Produits Chimiques de Croissy, Ltd., German Pat. 210,012 (1907).

<sup>6</sup> Chem. Fabriken Dr. K. Albert, German Pat. Application C. 27,625, Class 12q (4th October, 1918).

<sup>7</sup> Remed, Czecko-Slov. Pat. 16,728; *Kunstst.*, 16, 207 (1926).

<sup>8</sup> E.g. reaction products from furfural and aromatic amines; see American Insulator Corp., U.S. Pat. 1,606,943; *C.* (1928), II, 295.

<sup>9</sup> See, for example, Knoll & Co., French Pats. 13,941-395,657.

suitable substance to be effected after the condensation with the phenolic substance. Combined products are thus obtained which offer certain advantages over mere mixtures of the corresponding resins.<sup>1</sup>

**Condensing Agents.** The condensation of formaldehyde with phenols is not merely accelerated by the presence of condensing agents, but the course of the reaction is also partially affected. The reaction can be carried out without the presence of any condensing agent, if required, but considerably more prolonged heating is then necessary. When using certain raw materials, however, the absence of special condensing agents is sometimes desirable.

Many years ago Story<sup>2</sup> patented a process of condensing phenols with formaldehyde in the absence of acids, which were then the usual condensing agents, by boiling under reflux 50 parts of commercial (95 per cent) carbolic acid with 30 parts of 40 per cent formaldehyde solution, usually for a period of about eight hours. The viscous product so produced was dehydrated, and if the condensation had not been carried too far, this then formed a clear transparent mass, capable of being hardened, which only remained soluble if the viscous condition was not lost by carrying the reaction too far. Reference to Fig. 5 (page 292) will show that the relatively short reaction period of eight hours can only be due to the presence of components of catalytic activity in the carbolic acid, such as pyridine bases.<sup>3</sup>

This is shown from the experiments of Redman, Weith, and Brock<sup>4</sup> on the production of an amber substitute, during which, in order to obtain the primary product, a pure phenol-formaldehyde charge, without condensing agents, had to be heated for 60 to 120 hours. Commercial cresol, on the other hand,

<sup>1</sup> Bakelite Corp., French Pats. 280,520-21; etc.

<sup>2</sup> German Pat. 173,990 (1905); *C.* (1906), II, 990; British Pat. 8,875 (1905); *Chem.-Ztg. Rep.* (1906), 298; see also French Pat. 353,995 and addition 9,861; Belgian Pat. 210,965; Handy, U.S. Pat. 1,287,299; *Kunstst.*, 10, 101 (1920).

<sup>3</sup> See also F. Pollak, *Ullmann's Encyclopaedia*, VII, 299; on the pyridine contents of "technical cresol," see C. Fischer and F. Koske, *Arch. Kais. Ges.-A.*, 19, 577 *et seq.*; *C.* (1903), I, 983.

<sup>4</sup> U.S. Pats. 1,310,087-8 (1919); 1,374,526 (1921); *C.* (1921), IV, 132; see also U.S. Pat. 1,358,394 (1919); *C.* (1921), II, 176.



required heating for 4 to 12 hours only, and crude cresol for 2 hours only, in order to form a viscous creamy layer of liquid resin. The reaction could be accelerated by heating to a higher temperature under pressure.<sup>1</sup>

A further increase in reactivity can be produced by the use of especially suitable raw materials, such as the very reactive m-cresol on the one hand,<sup>2</sup> and of highly concentrated formaldehyde on the other.<sup>3</sup>

In general, however, condensation without condensing agents leads to difficulties of many kinds, which cause the production of a primary product possessing but little capacity for being hardened, and necessitating the addition of further quantities of formaldehyde after condensation has been largely effected, by which means complete hardening is ensured. The difficulties referred to lead, for example, to difficulty in obtaining a solid, hardening product, which is still soluble, by further treatment.

The reaction between phenols and formaldehyde can be greatly accelerated by the addition of suitable condensing agents, which may be either acid or basic.<sup>4</sup> The most effective are mineral acids and caustic alkalis, of which extremely small amounts, for example, 0.1 per cent, calculated on the weight of phenol, lead to exceedingly rapid reaction. However, these substances are difficult to remove from the resin after the reaction and cause very bad effects in the final product, such as attack of the filling agent or support, hygroscopic properties, deterioration of the insulating power, and so forth.<sup>5</sup> Difficulties also frequently occur during actual

<sup>1</sup> See Aylsworth, U.S. Pats. 1,033,044; 1,102,630 (1914); German Pat. 258,250; *C.* (1913), I, 1481; German Pat. 307,892; *C.* (1918), II, 786; Condensite Co. of America, Austrian Pat. 99,124 (1921); *C.* (1926), II, 1477; *Kunstst.*, 16, 231 (1926).

<sup>2</sup> See p. 292.

<sup>3</sup> See p. 301.

<sup>4</sup> Neutral substances are ineffective; see also C. Matsumoto, *Kunstst.*, 5, 252 Ref. (1915); see, however, Verreries de Folembray, French Pat. 30,787, additional to French Pat. 563,777; *C.* (1926), II, 1595; (1928), II, 205; use of  $\text{CaCl}_2$ .

<sup>5</sup> On a process for the removal of the condensing agent by the electric current, see Ges. für Chem. Industrie, Basle, Swiss Pat. 125,012; *C.* (1928), II, 1155.

production, especially on the large scale. Innumerable other condensing agents have therefore been proposed, of which ammonia has perhaps attained the greatest practical importance. This reagent not only accelerates the reaction to a remarkable degree, but remains in the final product in firm combination with formaldehyde as hexamethylene-tetramine, a very feebly basic substance with a high decomposition temperature, which has also the power of fixing free phenols and of assisting the hardening process. The various condensing agents which have been suggested will now be briefly referred to.

**Basic Substances.** Solutions of caustic alkalies were already used for the production of soluble products from phenols and formaldehyde in 1903 by F. Henschke,<sup>1</sup> who recommended alkaline solutions of these products as disinfecting agents. For the production of hardening resins, Baekeland<sup>2</sup> used bases, such as ammonia,<sup>3</sup> ammonium carbonate, alkali hydroxides and carbonates, aniline,<sup>4</sup> pyridine, amines,<sup>5</sup> or basic salts, or salts which yield bases by secondary reactions, such as the sulphites, sulphides, acetates or cyanides of the alkali metals, sodium phosphate, borax and soaps. The proportion of base was not to amount to more than 10 per cent of the weight of phenol,<sup>6</sup> or not more than one-fifth of the amount necessary to form the phenolate. If a larger proportion of base is used, a corresponding proportion is neutralized before hardening.<sup>7</sup> Salts of neutral or alkaline reaction are also recommended.<sup>8</sup>

<sup>1</sup> German Pats. 157,553-4 (1903); *C.* (1905), I, 415; *Frdl.*, VII, 607; see also Stephan, U.S. Pat. 812,608 (1906).

<sup>2</sup> U.S. Pat. 942,699; Swiss Pats. 45,485-7; French Pat. 386,627; U.S. Pat. 942,809 (1909); *Kunstst.*, I, 171 (1911); British Pat. 21,566 (1908).

<sup>3</sup> On the production of insoluble condensation products from phenols and formaldehyde under the influence of ammonia for the production of disinfectants, see A. Speier, German Pat. 99,570 (1897); *Frdl.*, V, 723; *C.* (1899), I, 462.

<sup>4</sup> L. Helm, e.g. French Pat. 392,395; with addition 10,415.

<sup>5</sup> See also Walter, German Pat. 118,567; *C.* (1901), I, 652.

<sup>6</sup> Bakelite G.m.b.H., German Pat. 281,454 (1908); *C.* (1915), I, 238.

<sup>7</sup> Baekeland, U.S. Pat. 1,187,229 (1916); *Kunstst.*, 6, 282, 298 (1916); see also British Pat. 159,461.

<sup>8</sup> Bakelite G.m.b.H., German Pat. 228,639 (1907); *C.* (1910), II, 1843; *Kunstst.*, I, 56 (1911); U.S. Pat. 942,700; see also Knoll & Co., German Pat. 219,209 (1907); *C.* (1910), I, 973; *Kunstst.*, 2, 165 (1912); British Pat. 28,009 (1907); Swiss Pat. 41,910; French Pat. 395,657; see also Swiss Pat. 40,994.

such as potassium chromate, neutral sodium sulphite, ammonium sulphide, sodium thiosulphate, trisodium phosphate, sodium dicarbonate, sodium, potassium and ammonium carbonates or sodium acetate. In addition, especially in the non-German patents, a large number of processes are referred to in which the above mentioned condensing agents or similar products are used, usually in association with unimportant modifications of the main process.

The following are so used: sodium hydroxide solution,<sup>1</sup> sodium carbonate,<sup>2</sup> water glass,<sup>3</sup> sodium sulphite, neutral sulphites,<sup>4</sup> thiosulphate,<sup>5</sup> calcium cresolate,<sup>6</sup> sodium salicylate,<sup>7</sup> sodium glycerate,<sup>8</sup> neutral alkali salts of aromatic hydroxyacids (sodium potassium salicylate),<sup>9</sup> the ammonium, alkali or alkaline earth salts of sulphonic acids,<sup>10</sup> sodium tungstate,<sup>11</sup> soaps,<sup>12</sup> magnesium oxide or carbonate,<sup>13</sup> magnesium

<sup>1</sup> Claypoole, British Pat. 2,122 (1908); French Pat. 394,614; van Voorhout, U.S. Pats. 1,271,392-3 (1918); French Pat. 483,417 (1917); Robinson-Bindley, Weller, Dulcken, British Pat. 145,128 (1919); *Kunstst.*, 11, 15, 174 (1921).

<sup>2</sup> According to Lebach carbon dioxide is immediately liberated, for which reason sodium carbonate has the same action as the hydroxide. See also the Termitite Co., E. Roller, U.S. Pat. 1,532,952 (1920); *C.* (1925), II, 356, on essential containers for sodium carbonate.

<sup>3</sup> Regal, French Pat. 468,241 (1914); *Kunstst.*, 5, 69 (1915); Dutch Pat. 2,187 (1917); *Kunstst.*, 8, 45 (1918).

<sup>4</sup> Robinson-Bindley, Weller, Dulcken, British Pat. 134,564 (1918); *Kunstst.*, 10, 157 (1920); Scudder, Pettigrew, British Pat. 158,796 (1919); *C.* (1921), II, 372.

<sup>5</sup> Byrom, Attwater, British Pat. 192,941; *C.* (1923), IV, 669; *Kunstst.*, 13, 125 (1923); U.S. Pat. 1,472,353.

<sup>6</sup> Brown, Kendall, U.S. Pat. 1,263,031 (1918).

<sup>7</sup> W. Esch, German Pat. 305,538 (1917); *C.* (1919), IV, 622; see also German Pat. 352,594 (1915) Ges. für Technik m.b.H.; Jaloustre, Kheifetz, Warchaysky, British Pats. 138,061; 139,147 (1919); *Kunstst.*, 11, 6, 14 (1921).

<sup>8</sup> Heinemann, U.S. Pat. 1,441,981 (1923); British Pat. 184,984 (1921); see also Footnote p. 225 German copy.

<sup>9</sup> French Pat. 483,915 (1917); Danish Pat. 21,606 (1916); British Pat. 117,857 (1917); *Kunstst.*, 9, 94 (1919); U.S. Pat. 1,273,967.

<sup>10</sup> Tarassoff, Shestakoff, British Pat. 102,635 (1916); U.S. Pats. 1,235,507; 1,237,579.

<sup>11</sup> Achtmeyer, U.S. Pat. 1,429,265 (1922); *C.* (1923), IV, 668; *Kunstst.*, 13, 125 (1923); Canadian Pat. 240,528.

<sup>12</sup> Wenjact-Ges., German Pats. 351,104 (1915); 384,147 (1920); *Kunstst.*, 14, 28, 92 (1924); *C.* (1922), IV, 256; (1924), I, 221; French Pat. 448,330; *Kunstst.*, 3, 217 (1913); French Pat. 473,603; *Kunstst.*, 8, 45 (1918); British Pat. 20,986 (1912); *Kunstst.*, 4, 98, 159 (1914); Swiss Pat. 64,241 (1912); *Kunstst.*, 4, 238 (1914). Soap and hydrosulphite: C. Kulas, C. Pauling, Swiss Pat. 93,297 (1920).

<sup>13</sup> H. Römmeler, Akt.-Ges., German Pat. 359,826 (1919); *C.* (1923), II, 340; *Kunstst.*, 13, 44, 57 (1923).

hydroxide,<sup>1</sup> alkaline earth oxides,<sup>2</sup> ammonia,<sup>3</sup> hexamethylene tetramine, its salts and double compounds (not more than 2 per cent),<sup>4</sup> ammonium salts of volatile organic acids or ammonium bicarbonate,<sup>5</sup> ammonium sulphide (for pale resins),<sup>6</sup> amines (aniline) or ammonium salts,<sup>7</sup> aminophenols,<sup>8</sup> indophenols and indamines, dimethylaniline,<sup>9</sup> hydrazine (colourless resins),<sup>10</sup> phenyl hydrazine,<sup>11</sup> hydroxylamine,<sup>12</sup> pyridine,<sup>13</sup> and so forth; also superoxides<sup>14</sup> siccatives,<sup>15</sup> Activine (sodium salt of p-toluenesulphonchloramide),<sup>16</sup> and so forth.

After the condensation is completed the bases are sometimes neutralized. For this purpose, Aylsworth<sup>17</sup> uses organic acids, such as palmitic or stearic acid, or resin acids such as colophony. For the neutralization of alkaline earth oxides, sulphuric or carbonic acid are said to be used in order to obtain salts which are as inert as possible electrically, in order that their presence in the ultimate product may not be disadvantageous. Filhol<sup>18</sup> uses ethylsulphuric acid for neutralizing

<sup>1</sup> Ellis-Foster Co., C. Ellis, U.S. Pats. 1,580,424-5 (1923); *C.* (1926), I, 3577; *Kunstst.*, 16, 156 (1926); see also U.S. Pat. 1,536,253.

<sup>2</sup> Aylsworth, U.S. Pat. 1,111,288.

<sup>3</sup> Paqué, Australian Pat. 8,096 (1909); Wiechmann, U.S. Pat. 1,080,188 (1913); Kendall, U.S. Pat. 1,418,718; *C.* (1923), IV, 668; *Kunstst.*, 13, 125 (1923); caustic potash solution and ammonia: D. Rai, U.S. Pat. 1,483,368.

<sup>4</sup> Vickers, Ltd., Joco Rubber & Waterproofing Co., Ltd., W. H. Nuttall, British Pat. 160,258 (1919); *C.* (1921), IV, 132.

<sup>5</sup> Dior, British Pat. 124,010 (1919).

<sup>6</sup> Kunisch, French Pat. 426,568 (1911); *Kunstst.*, 1, 356 (1911); 2, 10 (1912).

<sup>7</sup> L. Helm, French Pat. 392,395, and addition 10,415; British Pat. 25,216 (1907); *Kunstst.*, 2, 94 (1912); Austrian Pat. 38,951.

<sup>8</sup> Felton & Guillaume Carlswerk A.-G., German Pat. 358,195 (1919); *Frdl.*, XIV, 1136; *C.* (1922), IV, 955.

<sup>9</sup> A. Regal, U.S. Pat. 1,584,472-3 (1925); *C.* (1926), II, 656; British Pat. 254,888 (1925); *C.* (1926), II, 2501; *Kunstst.*, 16, 231 (1926); German Pat. 441,708; 442,361; *C.* (1927), I, 2778.

<sup>10</sup> Vickers, Joco Rubber & Waterproofing Co., W. H. Nuttall, British Pat. 158,447 (1919); *C.* (1921), II, 964.

<sup>11</sup> A. Regal, German Pat. 442,361; *C.* (1927), I, 2278.

<sup>12</sup> Lebach, *J. Soc. Chem. Ind.*, 32, 560 (1913).

<sup>13</sup> Baekeland, U.S. Pat. 942,809 (1909).

<sup>14</sup> Siemens & Halske A.-G., J. Grüss, German Pat. 432,252 (1924); *C.* (1926), II, 1793.

<sup>15</sup> Westinghouse Electric & Manufacturing Co., U.S. Pats. 1,632,113; 1,633,976; *C.* (1928), II, 294.

<sup>16</sup> G. Petrow, British Pat. 283,002; French Pat. 628,130; *C.* (1928), II, 815.

<sup>17</sup> U.S. Pats. 1,146,300 (1915); 1,111,288.

<sup>18</sup> British Pat. 147,173 (1920).

ammonia. Organic acids, such as benzoic and salicylic acids, are also recommended.<sup>1</sup>

**Acids and other Reagents of Acid Character.** Acids and acid salts may be used with advantage for the production of fusible and permanently soluble phenol-formaldehyde resins, as was explained in the section dealing with the subject. (See page 280 *et seq.*) If large proportions of formaldehyde are used, however, insoluble and infusible products are obtained; these products were frequently obtained at the time when the scientific investigation of these processes was in its infancy; their production is not surprising in the presence of such condensing agents as strong mineral acids. For the production of hardening resins, basic condensing agents are more suitable than those of acid character, although the latter have been proposed for certain processes. Acids were more especially used as condensing agents in the first technical attempts to exploit the phenol-formaldehyde condensation, and their energetic action was moderated by the addition of solvents, either during the initial condensation (Smith),<sup>2</sup> or during the hardening process (Luft).<sup>3</sup> A. T. and F. E. Birkby<sup>4</sup> carry out the condensation of phenols with formaldehyde in the presence of dilute sulphuric acid, which is neutralized by the addition of lime after the reaction.<sup>5</sup> A similar action is presumably exerted by such condensing agents as acid salts,<sup>6</sup> and the chlorides, sulphates and phthallates of hexamethylene tetramine,<sup>7</sup> and also by such substances as the chlorides of zinc and aluminium,<sup>8</sup> stannous chloride,<sup>9</sup>

<sup>1</sup> Wenjacet Gesellschaft, German Pat. 351,104; on the use of lactic acid for neutralizing  $\text{CaCO}_3$ , see G. A. Lacroix, French Pat. 623,535; *C.* (1928), II, 294.

<sup>2</sup> German Pat. 112,685 (1899); *Chem. Ztg.* (1900), 740; British Pat. 16,247 (1899); U.S. Pat. 643,012 (1900); Austrian Pat. 3,198.

<sup>3</sup> German Pat. 140,552 (1902); *Chem. Ztg.* (1903), 374; French Pat. 735,278 (1903); French Pat. 320,991; Austrian Pat. 14,037; British Pat. 10,218 (1902).

<sup>4</sup> British Pat. 153,494 (1920); *C.* (1921), II, 362.

<sup>5</sup> See also Aylsworth, U.S. Pat. 1,197,171 (1916); *Kunstst.*, 7, 52 (1917); on the use of oxalic acid, which is finally neutralized, for example, by calcium carbonate, see Allgem. Elektrizitäts-Ges., German Pat. Application A, 30,190, Class 22h (16th February, 1918.)

<sup>6</sup> Knoll & Co., German Pat. 219,209 (1907); *Frdl.*, IX, 1120; *C.* (1910), I, 973.

<sup>7</sup> British Pat., 160,258 (1919).

<sup>8</sup> General Electric Co., French Pat. 406,686 (1909).

<sup>9</sup> American Cellulose and Chem. Manuf. Co., Ltd., G. W. Miles, U.S. Pat. 1,549,888 (1924); *C.* (1926), I, 251; *Kunstst.*, 16, 75 (1926).

ferric chloride,<sup>1</sup> calcium chloride,<sup>2</sup> lead acetate,<sup>3</sup> sulphur dioxide,<sup>4</sup> carbon dioxide,<sup>5</sup> chlorine (followed by Chile nitrate)<sup>6</sup> phosphorus pentachloride,<sup>7</sup> salts of bromine,<sup>8</sup> ozone,<sup>9</sup> degradation products of cellulose (from oxycellulose and calcium hypochlorite)<sup>10</sup> bleaching powder,<sup>11</sup> and so forth. Other condensing agents which are employed are chlorinated hydrocarbons,<sup>12</sup> sulphonated rosin oils,<sup>13</sup> aromatic sulpho-fatty acids or naphtha-sulphonic acids,<sup>14</sup> naphthalene- $\alpha$ -sulphonic acid,<sup>15</sup> the neutral esters of strong acids,<sup>16</sup> chloramino-aldehydes,<sup>17</sup> toluenesulphochloramide,<sup>18</sup> and acids which decompose, or the salts of amines, such as aniline acetate, which are converted into inert materials during the hardening process.<sup>19</sup>

<sup>1</sup> Stockhausen, Gruhl, British Pat. 14,481 (1913); U.S. Pat. 1,150,642 (1915); French Pat. 460,675; Swiss Pat. 66,513.

<sup>2</sup> Soc. des Verreries de Folembay, French Pat. 563,777 (1922); *C.* (1926), II, 1595.

<sup>3</sup> Grigori Petrow, German Pat. 442,211; *C.* (1927), II, 645.

<sup>4</sup> Sarason, German Pat. 219,570 (1908); see p. 279; Heinemann, Harvey, Robinson, British Pat. 28,187 (1913); *Kunstst.*, 6, 86 (1916); Heinemann, British Pat. 9,390 (1914); *Kunstst.*, 6, 73 (1916); Smith, German Pat. 112,685 (1899); *Chem. Ztg.* (1900), 740.

<sup>5</sup> McCoy, U.S. Pats. 1,253,261-2 (1918); 1,253,404 (1918).

<sup>6</sup> Allgem. Elektrizitäts-Ges., German Pat. 273,261 (1912); *Kunstst.*, 4, 213 (1914); *C.* (1914), I, 1794.

<sup>7</sup> E. Ropp, French Pat. 564,575 (1922); *C.* (1926), II, 1595.

<sup>8</sup> R. Mannesmann, Swiss Pat. 87,046 (1919); *C.* (1921), II, 362; *Kunstst.*, II, 71 (1921).

<sup>9</sup> Regal & Co., J. Novak, J. Kostal, German Pat. 429,043; Austrian Pat. 100,205 (1924); *C.* (1926), II, 1207.

<sup>10</sup> W. Hunter, Fairgrieve, W. Tod, Jr. & Co., Canadian Pat. 245,651 (1924); *C.* (1926), I, 250; *Kunstst.*, 16, 117 (1926); British Pat. 218,793 (1923); *C.* (1926), II, 113; U.S. Pat. 1,579,112; French Pat. 581,705; Austrian Pat. 102,795; *C.* (1928), I, 122; German Pat. 458,105; *C.* (1928), I, 2464.

<sup>11</sup> R. Arnot, German Pat. 418,732 (1924); *C.* (1926), I, 1915.

<sup>12</sup> Mannesmann, Swiss Pat. 79,962; *Kunstst.*, 9, 261 (1919); Swiss Pat. 85,870; *Kunstst.*, 11, 47 (1921); Bauunternehmungen G.m.b.H., German Pat. Application S. 46,439, Class 30b (16th March, 1917).

<sup>13</sup> K. Tarassoff, German Pat. 367,239 (1914); *C.* (1923), II, 863; *Kunstst.*, 13, 34, 89 (1923); British Pats. 6, 716 (1914); 7,560 (1914); 102,751; U.S. Pat. 1,235,507; *Kunstst.*, 6, 205 (1916); 7, 162, 309 (1917); 8, 57 (1918); II, 166 (1921).

<sup>14</sup> G. Petroff, German Pat. 407,002 (1922); *Kunstst.*, 15, 165 (1925); *C.* (1925), I, 1818; *Frdl.*, XIV, 1142; on the product known as "Carbolite," see *Kunstst.*, 18, 81, 107, 124 (1926) and 16, 251 (1926); 17, 65 (1927).

<sup>15</sup> G. Danilowitsch, G. Petroff, German Pat. 418,198 (1924); *C.* (1926), I, 251; *Kunstst.*, 16, 76 (1926); British Pat. 231,501.

<sup>16</sup> Martinet, Vacher, French Pat. 538,450; *C.* (1923), IV, 730; *Kunstst.*, 13, 125 (1923).

<sup>17</sup> Regal & Co., R. Singer, U.S. Pat., 1,590,961 (1925); *C.* (1926), II, 1207.

<sup>18</sup> G. Petroff, British Pat. 283,002.

<sup>19</sup> C. Kulas, J. Scheiber, German Pat. 432,152 (1924); *C.* (1926), II, 1792.

The recommendation has also been made to effect the reaction in stages, a separate condensing agent being employed for each. Thus, Claypoole<sup>1</sup> recommends that the condensation should be effected in the presence of acid, which is then neutralized, after which the material is concentrated by evaporation and finally hardened in the presence of a base. According to another process condensation is carried out after the addition of acid, and after condensation fresh quantities of phenol and formaldehyde are added, and the mixture further condensed to form the hardening phenol-formaldehyde resin in a basic medium.<sup>2</sup> It is alleged that by these means less formaldehyde is used. Condensation in stages with interposed washing operations has also been proposed.<sup>3</sup> On the production of phenol-formaldehyde resins under the influence of electrolysis, see French Pat. 518,600 (1919);<sup>4</sup> on the influence of the silent electric discharge, see U.S. Pat. 1,473,347 (1921).<sup>5</sup>

**Various Added Materials.** The insoluble and infusible final products obtainable from the hardening phenol-formaldehyde resins are extremely hard materials, which show a fair amount of elasticity under certain conditions, but usually products are obtained which have insufficient resistance to stresses, and especially to longitudinal stress and percussion. These deficiencies can frequently be overcome by the addition of suitable fillers, especially those of a fibrous character. When, however, no such materials may be added, as is more especially the case for materials which are to be employed for casting, the elasticity must be improved by the addition of certain substances which possess solvent power, i.e. which act, so to say, as dispersion agents in the gel which is produced, and which greatly

<sup>1</sup> British Pat. 2,122 (1908); French Pat. 394,614.

<sup>2</sup> C. Kulas, C. Pauling, German Pat. 414,959 (1920); *C.* (1925), II, 1232; German Pat. 424,074 (1921); *C.* (1926), I, 2152; *Kunstst.*, 16, 117 (1926); German Pat. 431,619 (1922); *C.* (1926), II, 1467; *Kunstst.*, 16, 254 (1926); British Pat. 159,494 (1920); *C.* (1921), IV, 133; British Pat. 191,417; *C.* (1923), IV, 599; U.S. Pat. 1,414,139 (1922); 1,582,056; Swiss Pats. 93,297; 94,616; 106,557 (1923); Canadian Pat. 240,145 (1923); French Pat. 540,297; Danish Pat. 29,472.

<sup>3</sup> E.g. see E. E. Walker, British Pat. 259,046; *C.* (1928), II, 294.

<sup>4</sup> Resan Kunsthharzerzeugungs-Ges., *C.* (1921), IV, 912; British Pat. 130,608, Swiss Pat. 90,710; *Kunstst.*, 12, 38, 39 (1922); Austrian Pat. Application A, 1609-18, Class 39b (22nd February, 1918).

<sup>5</sup> W. Hoskins, *C.* (1926), II, 1470; *Kunstst.*, 16, 254, (1926).

influence, as such, its mechanical properties. Some of the substances which are employed are themselves capable of reacting with formaldehyde or with phenols, such as glycerine, casein, glue, and so forth. Others do not interact chemically with formaldehyde-phenol condensation products or their components. The substances which are used are ordinarily incorporated after the formation of the initial condensation product; there are, however, processes in which such substances are dissolved or caused to interact chemically with one or the other component or their mixtures.

In the accounts of the first attempts to produce hardening phenol-formaldehyde resins the most important additions are already mentioned, such as 5 to 10 per cent of natural resins (Smith), camphor, rubber, glycerine, and so forth (Luft), and fatty oils, such as castor oil, olive oil, almond oil, turnip oil, and so forth, and also pitch (Story). The following are also mentioned later: kieselguhr, talc, starch, casein, pigments (Bakelite G.m.b.H.),<sup>1</sup> resins, camphor, camphor substitutes, cellulose, esters, organic and mineral pigments (Knoll & Co.),<sup>2</sup> clove oil, soap, shellac, small amounts of paraffins, benzene hydrocarbons (Claypoole),<sup>3</sup> amyl alcohol (Smith), and so forth. These and other similar additions are referred to in later patent specifications, with considerable regularity. In the following account, therefore, those processes only will be dealt with which devote special attention to the substance in question. Authentic information on the specific suitability of these various materials has not yet been published,<sup>4</sup> and a detailed description may therefore be dispensed with.

<sup>1</sup> German Pat. 228,639.

<sup>2</sup> British Pat. 28,009 (1908).

<sup>3</sup> British Pat. 2,122 (1908).

<sup>4</sup> Bottler, *Kunstharze*, Leipzig and Munich (1919), p. 37, refers to the results of investigations by the Vienna Research Institute for Chemical Industry, according to which small additions of calcium oxide and zinc oxide to a so-called "acid resin" from phenol and formaldehyde reduced the brittleness satisfactorily without any decrease in the hardness. On the other hand, the brittleness was not reduced by the addition of various mineral oils and rosin oils. "The best results were obtained by the addition to the acid resin of various organic bases, such as aniline, diphenylamine, phenylene diamine, or naphthylamine in small amount." An "alkaline resin" which was similarly tested showed no such improvement. It is impossible to gather from the citation whether the resins were of the hardening type or not; moreover, part of the observed effects may be due to the action of the added substances as active fillers, that is, as contact agents.



Among other substances which are used are the following: hydrocarbons, such as naphthalene, nitrobenzene, and so forth;<sup>1</sup> chloronaphthalenes,<sup>2</sup> chlorophenols,<sup>3</sup> unsubstituted phenols,<sup>4</sup> cresyl phosphates,<sup>5</sup> anhydroformaldehydeaniline and aniline,<sup>6</sup> glycerine,<sup>7</sup> alkali glycerate,<sup>8</sup> lactic acid,<sup>9</sup> anhydrides of organic acids,<sup>10</sup> benzoic acid, salicylic acid,<sup>11</sup> also cumarone resins,<sup>12</sup> other resins,<sup>13</sup> glycerine-phthalic acid resins,<sup>14</sup> phthalic esters,<sup>15</sup> permanently fusible resins, for example,

<sup>1</sup> Baekeland, U.S. Pat. 1,156,452 (1915); *Kunstst.*, 6, 12 (1916); U.S. Pat. 1,216,265 (1917), "Neutral oil"; U.S. Pats. 1,259,472-3 (1918); also anthracene and liquid hydrocarbons, such as toluene, xylene, and cumene, which are capable of dissolving the resins in the presence of naphthalene.

<sup>2</sup> Aylsworth, U.S. Pat. 1,087,422 (1914); *Kunstst.*, 4, 238 (1914); U.S. Pat. 1,111,285 (1914); acetanilide, castor oil, dinitrobenzene, and so forth, may also be used; see also U.S. Pat. 1,090,439 (1914); *Kunstst.*, 4, 275 (1914); Mannesmann, Danish Pat. 24,697 (1919).

<sup>3</sup> Aylsworth, U.S. Pats. 1,046,137 (1913); 1,046,420, 1,102,634; British Pat. 9,559 (1911); *Kunstst.*, 2, 316 (1912); French Pat. 429,292 (1911); German Pat. 307,892 (1911); *Frdl.* XIII, 649; *C.* (1918), II, 786; *Kunstst.*, 8, 305 (1918).

<sup>4</sup> Aylsworth, U.S. Pat. 1,090,439.

<sup>5</sup> Baekeland, U.S. Pat. 1,439,056 (1922); *C.* (1926), II, 1468; *Kunstst.*, 16, 253 (1926).

<sup>6</sup> Baekeland, U.S. Pat. 1,133,083 (1915); 1,216,265-6 (1917); 1,217,115 (1917); together with hydrocarbons or chlorinated hydrocarbons; see also Goldsmith, U.S. Pat. 1,228,428 (1917); also U.S. Pat. 1,168,626, 1,188,239; 1,230,829.

<sup>7</sup> Faville French Pat. 335 584 (1903); Les Produits Chimiques de Croissy, Swiss Pat. 43,633; L. Grognot, U.S. Pat. 906,219; Drummond, British Pat. 184,961 (1921); *C.* (1923), IV, 670; *Kunstst.*, 12, 175 (1922); 13, 125 (1923); Petroff, German Pat. 407,002 (1922); *C.* (1925), I, 1818; Dhanpat Rai, U.S. Pat. 1,483,368 (1923); *C.* (1925), I, 580.

<sup>8</sup> Bakelite G.m.b.H., German Pat. 377,188 (1919); *C.* (1923), IV, 603; *Frdl.* XIV, 1141; A. Heinemann, French Pat. 538 605; *C.* (1923), II, 863; *Kunstst.*, 13, 90 (1923); U.S. Pat. 1,441,981 (1921); *C.* (1924), I, 517; British Pat. 184,984 (1921); *Kunstst.*, 12, 175 (1922).

<sup>9</sup> Petersen, Clark, British Pat. 179,586 (1921); Sato, British Pat. 182,886 (1921); *C.* (1923), IV, 669; *Kunstst.*, 13, 125 (1923); Canadian Pat. 233,598.

<sup>10</sup> Aylsworth U.S. Pats. 1,020,594 (1912); 1,046,420 (1912); 1,102,634 (1914); *Kunstst.*, 2, 256 (1912); 3, 116 (1913).

<sup>11</sup> Wenjacet Ges.m.b.H., German Pat. 351,104 (1915); *Kunstst.*, 12, 133 (1922); see also German Pat. 384,147 (1920); *Kunstst.*, 14, 28, 92 (1924); *C.* (1922), IV, 256; (1924), I, 2211; colophony, montan resin, ceresine, naphthalene, or chlorinated naphthalenes.

<sup>12</sup> McCoy, U.S. Pat. 1,425,784 (1922); indene resins, polymerized wood oil.

<sup>13</sup> Japanlack: Hatta, Nakajima, Kaisha, Japanese Pat. 39,310 (1921); natural resins: E. Jäck, Swiss Pat. 107,630 (1924); French Pat. 591,637 (1925); *C.* (1926), II, 1476; *Kunstst.*, 16, 255 (1926).

<sup>14</sup> The Barrett Co., L. Weisberg, U.S. Pat. 1,443,935 (1921); *C.* (1925), I, 2731; *Kunstst.*, 15, 181 (1925).

<sup>15</sup> Selden Co., C. Conover, U.S. Pat. 1,592,082; *C.* (1926), II, 2120.

from phenol and formaldehyde,<sup>1</sup> creosote oil,<sup>2</sup> residues from the production of synthetic phenols,<sup>3</sup> turpentine oil,<sup>4</sup> turpentine oil and glycerine,<sup>5</sup> cellulose esters,<sup>6</sup> acetic esters of glycerine, cellulose, and so forth; mineral oil or tar oils and emulsifying agents,<sup>7</sup> oleic acid,<sup>8</sup> castor oil and other fatty oils,<sup>9</sup> oxidized,<sup>10</sup> saponified,<sup>11</sup> or sulphonated oils,<sup>12</sup> factis,<sup>13</sup> stearine pitch,<sup>14</sup>

<sup>1</sup> Baekeland, U.S. Pats. 1,306,681 (1919); 1,401,953 (1922); see also U.S. Pats. 1,259,472-3 (1918), and 1,156,452 (1915).

<sup>2</sup> Redman, U.S. Pats. 1,242,592-3; *Kunstst.*, 8, 143 (1918); British Pat. 119,252-3; *Kunstst.*, 10, 101 (1920).

<sup>3</sup> Hutin, Dauphin, French Pat. 491,264; *Kunstst.*, 10, 165 (1920).

<sup>4</sup> Tarassoff, Shestakoff, British Pat. 104,887 (1916); U.S. Pat. 1,252,507 (1918); also other terpenes, tars, etc., see also K. Tarassoff, British Pat. 223,636; French Pat. 568,925 (1923); *C.* (1926), II, 1475; *Kunstst.*, 16, 254 (1926).

<sup>5</sup> Van Voorhout, French Pat. 423,417 (1917); U.S. Pat. 1,271,393; *Kunstst.*, 10, 92 (1920).

<sup>6</sup> L. Collardon, Belgian Pat. 252,906; French Pat. 453,393; Swiss Pat. 63,821; *Kunstst.*, 3, 276, 355 (1913); 4, 216 (1914); Aylsworth, U.S. Pat. 1,094,830 (1914); Bonner, U.S. Pat. 1,173,337 (1916); Jones, U.S. Pat. 1,209,165 (1916); Weller, Robinson-Bindley, British Pat. 152,384 (1919); *Kunstst.*, 11, 37 (1921); U.S. Pat. 1,868,867 (1921); *C.* (1921), II, 267, 857; Dupont, British Pat. 168,838 (1918).

<sup>7</sup> G. Petroff, German Pats. 424,951 (1921); 437,612 (1924); Australian Pats. 8,622-3; British Pat. 203,124; 205,167; French Pats. 553,755-6 (1922); *C.* (1926), I, 2853, II, 1471; (1927), I, 530; *Kunstst.*, 16, 255 (1926).

<sup>8</sup> Chappell, U.S. Pat. 1,102,473 (1914).

<sup>9</sup> Robinson, British Pat. 136,298 (1918); *Kunstst.*, 10, 158 (1920); French Pat. 520,365 (1920); *C.* (1921), IV, 810; see also the interesting method of A. H. Brown, Siluminite Insulator Co., Ltd., British Pat. 255,516 (1925); *C.* (1926), II, 2501; Bakelite Cor., L. C. Byck, U.S. Pat. 1,590,079; Westinghouse Electric & Manufacturing Co., U.S. Pat. 1,633,976; *C.* (1928), II, 294.

<sup>10</sup> Caroselli, U.S. Pat. 1,086,139 (1914); *Kunstst.*, 4, 275 (1914); Chem. Fabrik Flörsheim, Dr. H. Noerdlinger, German Pats. 253,517-8 (1910); *Kunstst.*, 3, 17 (1913); French Pat. 444,026 with addition 15,927; *Kunstst.*, 3, 56, 57 (1913).

<sup>11</sup> Wennagel, U.S. Pats. 1,107,003 (1914); 1,197,316 (1916); British Pat. 20,986 (1912); also saponified rosin (colophony); Reeser, French Pat. 479,319 (1915); *Kunstst.*, 7, 27, 52, 66 (1917); 8, 42 (1918); British Pat. 10,055 (1915).

<sup>12</sup> Tarassoff, British Pats. 528, 6,716, 7,560 (1914); French Pats. 469,832, 470,810 (1914); U.S. Pat. 1,187,869; *Kunstst.*, 6, 283 (1916); U.S. Pats. 1,216,515-6 (1917); also sulphonated resin oils, U.S. Pat. 1,235,507 (1917); German Pat. 367,239 (1914); *C.* (1923), II, 863; *Kunstst.*, 13, 34, 89 (1923).

<sup>13</sup> J. J. Buser, German Pat. 273,192 (1913); *Frdl.* XI, 857; *C.* (1914), I, 1720; *Kunstst.*, 4, 214 (1914); French Pat. 458,904; *Kunstst.*, 4, 56 (1914); Swiss Pat. 65,927; *Kunstst.*, 5, 56 (1915); McCoy, U.S. Pat., 1,194,201 (1916); *Kunstst.*, 7, 9 (1917); British Pat. 13,657 (1913).

<sup>14</sup> Barringer, U.S. Pat. 1,091,621 (1914).

naphthenic acids,<sup>1</sup> viscose and similar products,<sup>2</sup> starch,<sup>3</sup> gelatine,<sup>4</sup> glue,<sup>5</sup> casein,<sup>6</sup> vegetable proteins,<sup>7</sup> albumens,<sup>8</sup> partially hydrolysed gelatine, albumens, and so forth,<sup>9</sup> ox blood serum,<sup>10</sup> and other substances. Recently, the resins from aromatic sulphamides and formaldehyde<sup>11</sup> and furfurol<sup>12</sup> have also been proposed.

The above-mentioned filling materials not only serve to endow the final product with greater elasticity, but also frequently serve to reduce the price. Also, in their capacity as diluents, they sometimes reduce the rapidity of hardening,<sup>13</sup> which is of special importance for such materials as are utilized for castings and which are then hardened in the moulds. Volatile solvents have also been added to the hardening phenol-formaldehyde condensation products for such purposes. If, for example, such a resin, when unmixed, soon hardens at 70° C., if mixed with considerable quantities of alcohol it may be boiled for several days under reflux without the formation of any insoluble material.

<sup>1</sup> G. Petroff, German Pat. 437,612; *C.* (1927), I, 530.

<sup>2</sup> Collardon, British Pat. 1,598 (1912); *Kunstst.*, 3, 295 (1913); Swedish Pat. 40,613 (1916); Taylor, U.S. Pat. 1,172,073 (1916); *Kunstst.*, 6, 196 (1916); Collardon, Austrian Pat. 82,803; *Kunstst.*, 11, 159 (1921); Bronnert, U.S. Pat. 1,374,718 (1921).

<sup>3</sup> Knoll & Co., French Pat. 397,051 (1908); British Pats. 27,096 (1908); 6,430 (1911); U.S. Pat. 965,823 (1910); Intosh, Canadian Pat. 229,396 (1922); *C.* (1924), I, 1717; *Kunstst.*, 14, 71 (1924); Diamond State Fibre Co., British Pat. 221,553.

<sup>4</sup> B. B. Goldsmith, U.S. Pat. 1,076,417 (1913); *Kunstst.*, 4, 174 (1914); Albuminoids; Stockhausen, German Pat. 277,653; *Chem.-Ztg. Rep.* (1914), 573; French Pat. 466,435 (1913); German Pat. 280,144 (1912); *Kunstst.*, 4, 238, 370 (1914); The Commercial Products Co., Ltd., Swiss Pat. 50,078; *Kunstst.*, 4, 368 (1914).

<sup>5</sup> Berend, U.S. Pat. 952,724 (1910); Büchner, Swiss Pat. 93,815 (1919); *Kunstst.*, 12, 164 (1922); R. Arnot, Canadian Pat. 256,883.

<sup>6</sup> Berend, U.S. Pat. 1,040,850 (1912); see also French Pat. 436,720 (1911); *Kunstst.*, 2, 255 (1912); 3, 97 (1913); B. B. Goldsmith, Austrian Pat. 43,463; *Kunstst.*, 1, 73 (1911); see also D. A. Spencer, H. D. Murray, *Journ. Soc. chem. Ind.*, 46, 637; *C.* (1927), II, 1756; albumen, casein, cellulose.

<sup>7</sup> Sato, U.S. Pats. 1,245,975-6-8-9, 1,245,980-1-2-3-4 (1917).

<sup>8</sup> B. B. Goldsmith, French Pat. 418,060; U.S. Pat. 965,137; *Kunstst.*, 1, 73, 235 (1911); Wiechmann, U.S. Pat. 1,061,346; *Kunstst.*, 3, 455 (1913); U.S. Pat. 1,135,340; *Kunstst.*, 5, 226 (1915).

<sup>9</sup> R. Arnot, British Pat. 225,953 (1923); *C.* (1925), I, 2049.

<sup>10</sup> H. Hagendorf, A. Breslauer, German Pats. 274,179 (1913); 288,347 (1914).

<sup>11</sup> Bakelite Corp., U.S. Pat. 1,650,109; *C.* (1928), II, 814.

<sup>12</sup> Bakelite Corp., U.S. Pat. 1,609,506; Canadian Pat. 261,953; *C.* (1928), II, 1040.

<sup>13</sup> Hexamethylene-tetramine is also recommended as a softening or plasticising agent; Ellis-Foster Co., C. Ellis, U.S. Pat. 1,579,195; *C.* (1926), II, 113

In the production of pressed mouldings such additions are also advantageous, in so far as they appreciably delay the hardening process and so enable the heat to penetrate better into the interior of the article, and thus promote the required transformations; the volatile substances which are produced are also thus afforded an opportunity of escaping through the outer layers, as these are not so rapidly converted into resite. On the other hand, in the case of additions of a comparatively volatile character there is danger of blister formation, unless the temperature of hardening is kept very low, which not only delays the whole process, but prevents the required and desirable degree of hardness and of chemical inertness from being attained. Many such additions, such as glycerine and phenol, considerably detract from the more desirable electrical properties of the product. Others, such as all hydrocarbons and their derivatives, prevent the formation of products of uniform character, on account of their high vapour pressure and consequent volatility; they also diminish the binding effect on any fillers which may be present. The addition of resins, cellulose, esters, rubber, and so forth, reduces the resistance to heat, which is one of the special advantages offered by resites.

**Further Modifications of the Processes.** Apart from the variations in the raw materials, condensing agents and other conditions, which we have already dealt with, modifications of the original process of production of hardening phenol-formaldehyde resins are mainly concerned with the purification of the condensation product and the removal of the water which it contains.<sup>1</sup>

Such measures were found to be particularly necessary when attention was directed to the production of pure phenol-formaldehyde products, free from condensing agents, from uncombined raw materials, such as phenol, and from any dyestuffs which might have been formed,<sup>2</sup> after these impurities had

<sup>1</sup> On the conduct of the reaction at lower temperatures at which it is not exothermic, see Wiechmann, U.S. Pat. 1,126,926; *Kunstst.*, 5, 129 (1915); on reactions between phenols and formaldehyde in presence of hydrocarbons, alcohol, and so forth, see Les Produits Chimiques de Croissy, French Pat. 392,978.

<sup>2</sup> On the formation of Aurine, see Trautenberg, *Angew.*, 36, 515 (1923).

been recognized to be responsible for dark coloration of the product and its instability to the action of light and air. Thus, Pollak<sup>1</sup> obtained pale final products, fast to light and air, by first producing initial condensation products with the smallest possible amounts of acid or basic condensing agents and then washing these systematically, first with water and then with organic solvents miscible with water, such as alcohols, ketones, and aldehydes,<sup>2</sup> and then hardening. According to another process, the substances which give rise to the production of coloured products are removed before hardening by extraction with suitable solvents such as ether.<sup>3</sup> Coralex<sup>4</sup> produced purified hardening resins by washing the crude primary condensation product from phenols and formaldehyde consecutively with hot water, dilute mineral acids and cold water. Purification by dissolving in alkali hydroxide solution and reprecipitation with acid is also recommended.<sup>5</sup> Finally, special attention should be directed to processes of purification of the condensation products in the form of their colloidal solutions. For this purpose the crude condensation products are peptonized by means of aqueous alkali hydroxide solutions of the highest possible concentration in quantity insufficient to form salts of the resin, with or without the presence of organic solvents. By precipitation by water or by solutions of salts which exert a hydrotropic effect, such as soap solutions,<sup>6</sup> or by salts, such as alum, sodium chloride, aluminium sulphate, and so forth,<sup>7</sup> the resins are then obtained in purified form, the impurities remaining in solution. In place of alkali hydroxides, oxides or

<sup>1</sup> German Pat. 394,253 (1919); *Frdl.* XIV, 1146; see also U.S. Pat. 1,369,352 (1914); *C.* (1921), IV, 809; British Pat. 20,977 (1914); *Kunstst.*, 6, 205 (1916); *II*, 183 (1921); Swiss Pat. 73,579; *Kunstst.*, 7, 36 (1917); Austrian Pat. 79,870; *Kunstst.*, 10, 182 (1920); French Pat. 510,603;

<sup>2</sup> The addition of a substance which oxidizes phenols is also recommended.

<sup>3</sup> Bakelite G.m.b.H., German Pat. 233,395 (1910); *C.* (1911), I, 1267; *Kunstst.*, 1, 174 (1911).

<sup>4</sup> British Pat. 148,264 (1919).

<sup>5</sup> The Damard Lacquer Co., V. Potter, French Pat. 520,364 (1920); *C.* (1921), IV, 809; British Pat. 131,112; *Kunstst.*, 10, 46 (1920); Coralex, French Pat. 528,442; *C.* (1922), IV, 955; and others.

<sup>6</sup> Bakelite G.m.b.H., German Pat. 431,514 (1925); *C.* (1926), II, 1465; *Kunstst.*, 16, 254 (1926).

<sup>7</sup> Bakelite G.m.b.H., F. Seebach, German Pat. 432,203 (1925); *C.* (1926), II, 2119; on the production of salts of resins by salting out, see H. Bucherer, German Pat. 350,043; *C.* (1922), IV, 157.

hydroxides of the alkaline earth metals or metallic phenol compounds may be employed.<sup>1</sup> The solutions of the resins in alkali may also be treated with acids in the presence of salts which exert a hydrotropic action.<sup>2</sup>

A method which unites a process of production with one by which the product is purified in alkaline solution, is represented by a process, the object of which is to produce resins free from phenols,<sup>3</sup> and which is similar to the methods of De Laire and of Blumer, with which we have already dealt. According to this process the phenol is used in alkaline solution, and is introduced in that form at 15° C., and with cooling, into a quantity of formaldehyde or acetaldehyde such that this is always present in excess throughout the reaction. The phenol-alcohols or poly-alcohols which are first obtained are then converted into resins by heating.

It is alleged that the phenols are more easily removed by washing if the resins are treated with de-gelatinizing agents, such as solutions of lactic acid.<sup>4</sup> It is also alleged that water and free phenols are easily removed by mixing monoacetin (glycerine-mono-acetate) containing free acetic acid with the resin and then fractionally distilling.<sup>5</sup> A final method remains to be mentioned, according to which colourless resins are stated to be obtained by treatment with carbon disulphide.<sup>6</sup>

The xanthogenic acid esters which are first formed are decomposed by acids after removing the impurities.

It is alleged that the phenol-formaldehyde resins, as first obtained, can be dehydrated by treatment with prodyl alcohol.<sup>7</sup>

<sup>1</sup> Bakelite G.m.b.H., F. Seebach, German Pat. 423,727 (1925); *C.* (1926), II, 2119.

<sup>2</sup> Bakelite G.m.b.H., German Pat. 432,202 (1925); *C.* (1926), II, 1792.

<sup>3</sup> Chem. Fabr., Dr. K. Albert, G.m.b.H., H. Amann, E. Fonrobert, U.S. Pat. 1,614,171; British Pat. 261,472; French Pat. 596,072; *C.* (1927), I, 1890; German Pat. Application C. 31,310, IV, 12q and C. 33,194, IV, 12q.

<sup>4</sup> O. Ehrlich, German Pat. 423,032 (1922); *C.* (1926), I, 3432.

<sup>5</sup> Siméon, French Pat. 540,336; *C.* (1923), IV, 670; *Kunstst.*, 13, 125 (1923).

<sup>6</sup> Camus, Duchemin, R. Berthon, French Pat. 522,150 (1919); *C.* (1921), IV, 872.

<sup>7</sup> Wenjacit-Ges. m.b.H., German Pat. 359,061 (1920); *Frdl.* XIV, 1134; *C.* (1923), II, 340; *Kunstst.*, 13, 44, 56 (1923).

The proposal has also been made to treat the finished resin with sulphur, sulphur chloride, and so forth.<sup>1</sup>

**Appliances for the Manufacture of Hardening Resins.** The ordinary manufacture of hardened phenol-formaldehyde resins, as described at the commencement of the chapter, is carried out in charges of several hundred kilograms. The following considerations must be allowed for in the design of the required plant. At first, during the reaction, which is initiated by warming the reaction mixture for a short time, considerable amounts of heat are liberated, and the temperature must therefore be controlled by suitable means of cooling; provision must also be made for sufficient reflux cooling of the vapours to prevent loss of the components and consequent alteration of the composition of the batch, as the temperature rise caused by the reaction leads to vigorous boiling of the reaction mixture. Further, the dehydration of the condensation product requires special precautions in consequence of the facility with which the hardening process proceeds in the product. The temperature may be maintained so low by distillation under pressure that the danger of premature hardening of the mass, with consequent insolubility and infusibility, is avoided; but as the hardening process is also exothermic it is necessary to provide for rapid cooling of the mass after this has been sufficiently dehydrated, in order that the hardening process may not occur through internal heat evolution.

Finally, the constructional material of the reaction vessel is important, more particularly for the colour of the products. Vessels of iron, lead or aluminium can ordinarily not be used. Copper vessels impart a slight dark coloration to the products, especially if ammonia is used as a condensing agent. Enamelled or tinned iron vessels or tinned copper or nickel vessels are suitable for the production of pale resins.<sup>2</sup>

A detailed description of the plant is impossible here, as its design greatly affects the results obtained and must, therefore,

<sup>1</sup> A. Samuel, French Pat. 549,811; *C.* (1923), IV, 574; see also *Compt. rend.*, 182, 206 (1926); *C.* (1926), I, 2728; the product is sold as "Thiolite"; see also Société "La Thiolite," Swiss Pats. 102,985; 125,975; German Pat. 447,000; W. Nagel, *Angew.*, 41, 685 (1928).

<sup>2</sup> Aylsworth, U.S. Pat. 1,102,630 (1914).

be kept very secret. For the production of Novolaks, any vessel capable of being heated, which is provided with an arrangement for securing a good draught, or still better, with a hood provided with a reflux condenser, may be used. For the manufacture of resoles, however, a number of details are of decisive importance, such as the dimensions of the hood, the relative proportions of diameter of reaction vessel to height of batch, shape of the bottom, dimensions of the exit pipe leading to the condensing plant, stirring gear, diameter of outlet valve, and so forth. All these details and many others are only settled by practical experience, and after commencing manufacture in a plant it is usually found necessary to make a number of alterations before satisfactory results are obtained. The arrangement of the control platform is also of great importance, as during the process continual alterations have to be made in the steam supply, supply of cooling water, degree of vacuum, and so forth, whilst the reaction mass must be continuously watched through sight glasses.

The preparation of the actual composition to be used for the manufacture of resite articles also requires special plant, the main necessity being that of completing the condensation process without giving too much opportunity for polymerization to occur. The plant must be designed in accordance with these requirements and with the varying composition of the reaction mixtures used for these purposes, and must be served by skilled operatives. The size of the batches is of special importance and must generally be kept very small.

Proposals have recently been made to manufacture resole products by a continuous process,<sup>1</sup> by passing the reaction mixture through a heating appliance and then dehydrating by special methods. Especially favourable results are said to be attained by maintaining a small portion only of the reaction mass in contact with a large surface on which it is exposed to the heating action throughout a short interval. Roller-driers may, for example, be used. In consequence of the greater ease

<sup>1</sup> C. Kulas, J. Scheiber, German Pat. 436,779 (1924); *Farb. und Lack* (1927), 126; British Pat. 230,861; French Pat. 594,932; Swiss Pat. 116,160; *C.* (1927), I, 529; C. Kulas, U.S. Pat. 1,669,831; *C.* (1928), II, 1392; Bakelite Corp., U.S. Pat. 1,660,403; *C.* (1928), II, 814.



with which distillation is effected, the process is characterized by the fact that impure raw materials, such as low temperature tar, may be used, without interference with the production of odourless, water-free, hard resoles of high melting point.<sup>1</sup>

It should be noted that it is necessary for economic operation that the condensed water from the distillates, the wash water, and the cooling water should be rationally dealt with,<sup>2</sup> and that the design of the plant must comply with these necessities.

**Properties of Resoles.** The hardening phenol-formaldehyde resins, or resoles, are used in considerable quantities. They are sold under various registered trade names, such as Bakelite A, Resinite, Redmanol, Sipilite, Condensite, Amberite, Faturan, Phenoform, Nuloid, Amberdeen, Formite, Issolith, Kopan, hardening Albertols, and so forth, some of these being obtainable in more than one quality.<sup>3</sup> Most of them are brownish yellow to dark brown liquid or solid transparent products, and are completely soluble in alcohol, butyl alcohol, amyl alcohol, glycerine, phenols, ether, acetone, esters, and sodium hydroxide solution, but are insoluble in benzene hydrocarbons, turpentine oil, fatty oils, and so forth. They generally possess a slight odour of phenol, due to the presence of very small amounts of that substance.<sup>4</sup> The presence of free formaldehyde is also sometimes noticeable.

The solid phenol-formaldehyde resins resemble colophony in appearance. Their melting and softening points usually lie between 50° and 70° C. Their specific gravity varies from about 1.18 to 1.19. On storage the resole resins maintain their solubility throughout a considerable period, but ripening processes occur which are associated with a rise of melting point to 80° C., or even to 90° C. Sometimes, the originally clear products develop cluster-like turbidities which are due to the

<sup>1</sup> On further proposals for improvement of plant, see Cie. Française pour l'Exploitation des Procédés Thomson-Houston, French Pat. 588,266 (1924); C. (1926), II, 1475; *Kunstst.*, 16, 255 (1926); A.E.G., German Pat. 459,310.

<sup>2</sup> E.g. see E. Glaser, Austrian Pat. 106,018; C. (1927), II, 1402.

<sup>3</sup> On German and non-German trade names, see *Kunstst.*, 15, 116 (1925).

<sup>4</sup> Latterly Resole qualities, for example, "Bakelite A," have been placed on the market, which are free from odour.

colloidal separation of water, due to continued condensation. The utility of the resins is not impaired by such changes.

The *liquid* phenol-formaldehyde resins represent products which are less completely condensed, of a specific gravity of about 1.14 to 1.20. On standing for a prolonged period, for example for some months, and particularly if kept warm, they

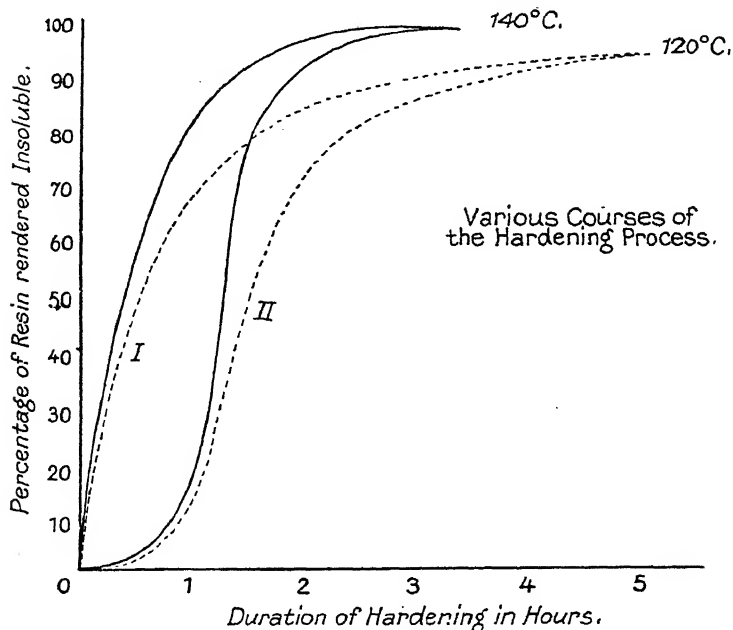


FIG. 6

show a tendency to thicken, accompanied by the separation of an aqueous layer at the surface, a process which is to be ascribed both to synergetic phenomena in the system resin-water, and to continued condensation. This change can be considerably retarded or even prevented by the addition of small amounts of spirit.

The hardening resins are also sold in the form of highly concentrated solutions, of various strengths, in spirit, as spirit varnishes or varnish oil substitutes.

The commercial products are usually completely free from those impurities which are ordinarily present in most natural resins. The ash content is usually negligible, being 0.1 per cent or less. (See page 390.) The exact character of the hardening quality is, of course, important, including the velocity and general course of the hardening process. A decision on the value of a sample must be based partly on the velocity of hardening, which must be suited to the intended application, and should not necessarily be very high, and also on the yield of hardened product and on its properties. (On valuation see page 393.)

For many applications the course of the hardening process is decisive; for some purposes, such as hot pressure moulding, resins with a high initial hardening velocity are to be preferred, whilst for other applications, such as the impregnation of paper for insulating wrappings, products are required, in which the hardening process is retarded, but which can ultimately be hardened to the same extent. The course of hardening in two products corresponding to these differing requirements is shown in the curves of Fig. 6.<sup>1</sup>

With regard to the chemical nature of resoles we refer the reader to pages 142 *et seq.*

#### APPLICATION OF RESOLES TO THE PRODUCTION OF HARDENED PHENOL-FORMALDEHYDE PRODUCTS

For the production of resite articles, other substances are used in addition to the commercial products referred to in the preceding section. Thus, for the production of substitutes for amber and other similar products, phenol-formaldehyde resins are employed which consist of intermediate products which do not keep well and which are capable of being intensively

<sup>1</sup> These curves are based on experiments by the authors. Both resins were prepared from 10 parts of crude cresol and 9 parts of 30% formaldehyde. The condensing agent used for Resin 1 was ammonia. Resin 2 was prepared by first condensing a portion of the cresol and of the formaldehyde with acid, then adding the remainder of the cresol and formaldehyde and completing the condensation with ammonia. Hardening was effected at 120° C. and at 140° C. The portion of the resin which had become insoluble was determined as the residue on extraction with a mixture of alcohol and acetone.

hardened; these are not marketed as such, but are supplied by the producing firms to fancy ware manufacturers, and so forth, in the form of hardened, insoluble and infusible masses in blocks or rods or in the form of rough castings.

The proposal has frequently been made to endow phenol-formaldehyde resins, or phenol-aldehyde resins in general, which have little or no hardening properties, with hardening properties, or improved hardening properties by the addition of formaldehyde, preferably in the polymerized condition, or of hexamethylene-tetramine or similar reactive substances.<sup>1</sup> Such a process was already described by Luft<sup>2</sup> in the form of the information that by the addition of glycerine, which had been saturated with formaldehyde vapour, a greater hardness of a hardening phenol-formaldehyde product could be achieved, or in other words, that a more rapid and intensive course of the hardening process could be attained. Among others, the following additions of this character have been proposed: polymers of formaldehyde, methylene-amines, more especially hexamethylene-tetramine, anhydroformaldehyde-aniline, hexamethylene-triphenol,<sup>3</sup> methylene chlorides, methylal and methylene acetate; other substances which have also been proposed are concentrated solutions of polymerized formaldehyde in cresol.<sup>4</sup>

<sup>1</sup> Aylsworth, German Pat. 307,892 (1911); *Frdl.* XIII, 649; U.S. Pat. 1,020,593; French Pat. 441,017; *Kunstst.*, 2, 355 (1912); U.S. Pat. 1,046,420; British Pats. 3496-8 (1911); U.S. Pat. 1,047,484; British Pat. 26,029 (1911); U.S. Pat. 1,090,439; French Pat. 463,192; Knoll & Co., French Pats. 13,940-1, additions to 397,051; *Kunstst.*, 1, 417 (1911); British Pat. 6,430 (1911); *Kunstst.*, 2, 316 (1912); Belgian Pat. 204,811; Baekeland, U.S. Pat. 1,038,475 (Phenolalcohols); *Kunstst.*, 3, 51 (1913); Austrian Pat. 56,950; Swiss Pat. 56,966; U.S. Pats. 1,216,265-6, 1,217,115; *Kunstst.*, 7, 261 (1917); Condensite Co., U.S. Pat. 1,115,766; *Kunstst.*, 5, 153 (1915); Aylsworth, Condensite Co., U.S. Pat. 1,137,374; *Kunstst.*, 5, 187 (1915); McCoy, U.S. Pat., 1,269,627; Baekeland, U.S. Pat. 1,354,154; *Kunstst.*, 11, 134 (1921); Redman, Weith, Brock, U.S. Pat. 1,358,394 (1919); *C.* (1921), II, 176; British Pat. 174,656; *Kunstst.*, 12, 142 (1922); U.S. Pat. 1,339,134; *Kunstst.*, 10, 167 (1920); Redman, Cheetham, U.S. Pat. 1,551,428; Ellis-Foster Co., C. Ellis, U.S. Pat. 1,579,195; Selden Co., C. Conover, U.S. Pat. 1,592,082 (Phthallic ester as hardening agent).

<sup>2</sup> German Pat. 140,552 (1920).

<sup>3</sup> L. H. Baekeland, U.S. Pat. 1,354,154 (1920).

<sup>4</sup> Chem. Fabr., Dr. Kurt Albert, German Pat. Application C. 29,929, 39b vom 7th December, 1920; on production of the solutions see German Pat. Application C. 27,625, IV, 12q.

The production of hardened products by treatment of less reactive phenol-formaldehyde resins of the Novolak or Saliretine type with hardening agents offers certain advantages over the use of resins which themselves possess sufficient hardening properties. In the first place, the fact must be emphasized that the manufacture of Novolak or Saliretine resins can be carried out without any difficulty, and more especially without any risk of the production of premature insolubility, which exists in the manufacture of hardening resin. Moreover, in the production of such products condensation can be carried to practical completion, so that the raw materials, especially the formaldehyde, can be utilized practically completely. Further, on account of their stable character, such resins can easily be produced free from impurities, such as free phenols, condensing agents, and so forth. Owing to their non-hardening character they may be stored for an indefinite period without danger of any loss of solubility. The admixture with the hardening agent can be undertaken in many ways and at any desired time, for example, by dry mixing or by joint solution in spirit immediately before use, but such solutions are generally not very stable on keeping. An advantage of considerable value consists in the simplicity of the procedure and the possibility of exact adjustment of the hardening agent, by which means the results can be varied at will.

On the other hand, the high price of such hardening agents as hexamethylene-tetramine must be taken into account, and also the circumstance that the condensation is in part effected at a later stage than usual, with the production of considerable amounts of volatile substances, such as water, ammonia, and so forth. From the last standpoint the use of anhydroformaldehyde-aniline is of great interest, as it yields no gases or easily volatile products during the hardening process, which is a matter of great importance for certain applications.

The part played by anhydroformaldehyde-aniline and similar substances as hardening agents was investigated by Baekeland.<sup>1</sup>

<sup>1</sup> U.S. Pat. 1,217,115; see also 1,216,265; see also Goldsmith, U.S. Pat. 1,168,626, 1,188,439, 1,228,428; *Kunstst.*, 6, 174, 282 (1916); 7, 323 (1917); 9, 137 (1919).

Naturally, the proportion of anhydroformaldehyde-aniline to Novolak has a considerable influence on the nature of the ultimate product. Mixtures containing not more than 20 parts by weight of anhydroformaldehyde-aniline per 100 parts by weight of fusible phenol-formaldehyde resin of the Novolak type, are still permanently fusible, even after heating for an indefinite period. A larger addition of anhydroformaldehyde-aniline, up to 200 parts by weight per 100 parts by weight of Novolak resin, yields products which become infusible on heating for some time, for example, to 160° C. These deep brown products are hardest when a proportion of about 110 to 130 parts of anhydroformaldehyde-aniline is used per 100 parts of Novolak resin. A larger addition causes increased plasticity at high temperatures. The resistance of the infusible products to chemical agents, such as alcohol, acetone, dilute caustic alkalies, and so forth, increases as the proportion of anhydroformaldehyde-aniline is increased.

The various phenol-formaldehyde products of Resole type are usually hardened by heating. The hardening process may be favourably influenced by certain other measures. Thus, the time of hardening (duration of heating) is considerably reduced in the presence of acids or of substances which are capable of liberating acids, such as acid chlorides, sulphuric acid esters, aluminium chloride, and so forth, or of acid salts; for this purpose the added acid may conveniently be dissolved in alcohol or glycerine.<sup>1</sup> The following substances are stated to act in a similar manner: ferric chloride,<sup>2</sup> ethylsulphuric acid,<sup>3</sup> reducing agents ( $H_2PO_2$ ) together with glycerine and a small amount of mineral acid,<sup>4</sup> glycerine esters, such as glycerine malonate and

<sup>1</sup> Knoll & Co., German Pat. 214,194 (1908); *C.* (1909), II, 1398; German Pat. 222,543 (1908); *C.* (1910), II, 124; U.S. Pat. 965,823 (H. Lebach); *Kunstst.*, 2, 10 (1912); Swiss Pat. 45,913; Austrian Pat. 45,474; British Pat. 27,096 (1908); French Pat. 397,051; see also Bruhat, British Pat. 129,993 (1919); 156,675 (1921); *C.* (1921), II, 808; *Kunstst.*, 11, 174 (1921); see also Eilertsen, British Pat. 165,758.

<sup>2</sup> Stockhausen, Gruhl, British Pat. 14,481 (1913); U.S. Pat. 1,150,642 (1915); French Pat. 460,675; Swiss Pat. 66,513; Belgian Pat. 261,327; *Kunstst.*, 4, 97, 379 (1914); 5, 56, 274 (1915).

<sup>3</sup> J. Fillhol, British Pat. 147,173 (1920); *C.* (1922), IV, 380; *Kunstst.*, 12, 133 (1922); U.S. Pat. 1,505,382.

<sup>4</sup> Lorival Manuf. Co., British Pat. 184,961; *C.* (1923), IV, 670.

so forth,<sup>1</sup> acid or basic metallic salts, such as copper sulphate or zinc chloride, and hydroxides, such as aluminium hydroxide.<sup>2</sup> It is also known that exceptionally hard and resistant end-products are obtained in the presence of strong alkalis, such as sodium and potassium hydroxides, which are stated to accelerate the hardening process also. The removal of the water formed in the hardening process by substances which unite with it,<sup>3</sup> or which interact with it, such as metallic carbides, nitrides, cyanamides, silicides or phosphides has also been proposed.<sup>4</sup>

The technical application of the hardening process is rendered particularly difficult by the fact that unless the temperature is raised with great care, blisters are easily formed. This difficulty constituted such an objection to the use of the hardening phenol-formaldehyde resins, that their successful technical application did not occur until Baekeland succeeded in overcoming it.<sup>5</sup> This advance was achieved by him by the simultaneous application of heat and pressure, to which the material was exposed until it became hard, infusible, and insoluble.<sup>6</sup> The hardening process is carried out in heated moulds, or in so-called "Bakelisers."<sup>7</sup> (See Fig. 7.) It was found later that by the use of suitable materials, end-products of high quality can also be obtained without the process just described, the hardening process being effected by careful heating only, without the application of pressure. For details see pages 339-340.

The resin which has been transformed into the final state, or hardened, by prolonged heating at 140° C. or more, and which

<sup>1</sup> J. Bruhat, French Pat. 575,532 (1923); *C.* (1926), II, 1596.

<sup>2</sup> Sato, Japanese Pat. 39,320 (1921); Baekeland had previously recommended the addition of zinc chloride, other metallic chlorides, acids or salts, for accelerating the hardening process, U.S. Pat. 942,699 (1907).

<sup>3</sup> Aylsworth, U.S. Pat. 1,102,630, phthalic anhydride, etc.; substances which are also capable of combining with ammonia; Allgem. Elektrizitätsges., German Pat. 271,825 (1911), gypsum, Portland cement, etc.

<sup>4</sup> Vickers, Ltd., Joco Rubber & Waterproofing Co., W. H. Nuttall, British Patent 154,656 (1919); *C.* (1921), II, 451.

<sup>5</sup> Leo Hendrik Baekeland, Life and Work, see *J. Ind. Chem.*, 8, 176; *Kunstst.*, 6, 241 (1916).

<sup>6</sup> L. H. Baekeland, German Pat. 233,803 (1908); *C.* (1911), I, 1391; British Pat. 1,921 (1908); U.S. Pat. 939,966, 942,699; French Pat. 386,627; Swiss Pat., 45,487; 45,785, 51,815.

<sup>7</sup> By kind permission of the Bakelite G.m.b.H., Charlottenburg-Erkner.

is known as resite,<sup>1</sup> may be either transparent, translucent, or opaque, and possesses a considerable degree of hardness; its specific gravity is about 1.25; it is insoluble in the ordinary solvents, and extremely resistant to chemical substances, such as oil, dilute acids, salt solutions, chlorine, hydrofluoric acid, steam, and so forth. It is attacked, to a very limited extent, by phenols, acetone, and pyridine. It is attacked more or less severely by oxidizing agents, such as nitric acid, chromic acid,

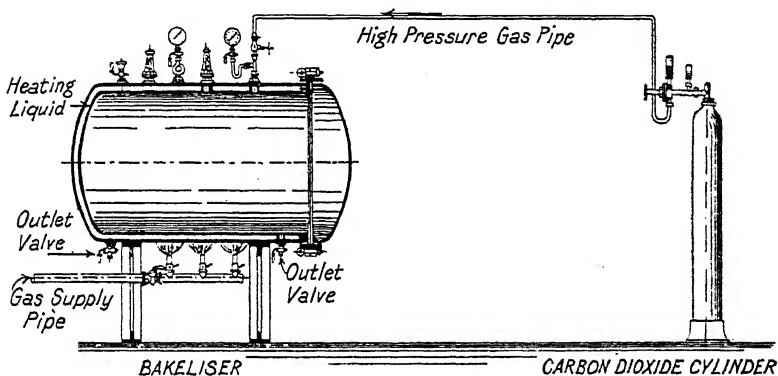


FIG 7

hot concentrated sulphuric acid, bromine iodine, and substances of alkaline reaction.<sup>2</sup> The resite mass is an excellent insulator of both heat and electricity, and is also distinguished by a high degree of resistance to mechanical influences, such as impact, friction, pressure, and so forth, and also against heat, moisture, and similar influences. On heating it does not melt, but at most softens slightly, and decomposes at temperatures exceeding 300° C.<sup>3</sup> The smell of phenol which occasionally clings to the unhardened resin is completely removed by the hardening process.

<sup>1</sup> The approximate composition is given by B. Casselmann, *Chem. Age* (1923), 443; *Kunstst.*, 14, 8 (1924), as C, 75.4%; H, 5.9%; and O, 18.7%.

<sup>2</sup> Lebach, *Angew.*, 38, 1092 (1925); G. S. Petroff, *Kunstst.*, 16, 251 (1926); 17, 65 (1927).

<sup>3</sup> On the effect of ageing, see E. J. Casselmann, *Chem. Age* (1923), 443; *Kunstst.*, 14, 8 (1924); *C.* (1924), I, 517, 2309; *Trans. Amer. Electr. Soc.*, 44, 153 (1923).



The change of electrical properties induced by hardening is of special interest. By experiments with a "pure Bakelite," Mannel showed<sup>1</sup> that the resistance increases with rising temperature, so that on heating to 204° C. the conductivity is reduced by 40 per cent of the original value. The electrical properties alter during hardening (Bakelization) as follows—

Duration of Heat Treatment (at. 105° C.) in hours	Dielectric Constant	Resistance. Ohms per sq. cm.	Breakdown Resistance. Volts 0.05 mm.
0	16.5	$17.2 \times 10^{11}$	1,450
0.5	3.8	$2.7 \times 10^{13}$	1,700
1	3.8	$4.3 \times 10^{14}$	1,950
1.5	3.8	—	2,000
2	4.0	$2 \times 10^{15}$	2,100
3	3.8	$2 \times 10^{15}$	3,100
4	4.9	$2 \times 10^{15}$	3,520
6	5.5	$2 \times 10^{15}$	3,520

According to the observations of Stäger,<sup>2</sup> the surface resistance is also essentially dependent on the degree of hardening of the resin, as in certain of the earlier stages thin surface layers of material which absorbs water are present, which increase the surface conductivity. Thus, on immersing in water for 24 hours, and treating in the manner prescribed by the VDE (Association of German Electrical Engineers), Stäger found the following decreases in the surface resistance—

Sample as submitted—	After 24 hours immersion in water—
(1) 6,788,000 megohms per sq. cm.	36,300 megohms per sq. cm.
(2) 37,340,000 " " "	266,100 " " "

In the finally hardened condition the electrical properties of the resin are subject to relatively slight changes only, and are very much less affected by temperature changes. A thermal

<sup>1</sup> *Arch. f. Elektrotech.*, 12, 497 (1924).

<sup>2</sup> See the section on the colloid chemistry of insulating materials in Liesegang's *Kolloidchemische Technologie*, Dresden and Leipzig (1926), p. 299. The V.D.E. regulations will be found in *Vorschriftenbuch des V.D.E.*, Springer, (1926); see also V.D.E. Bulletins 315, 318, and 318a, reproduced in the Appendix of this volume. On the velocity of absorption of water by Resite (Bakelite) products, see H. G. Leopold, J. Johnston, *Journ. phys. Chem.*, 32, 876; C. (1.28), II, 1722.

after-treatment of the products has, therefore, been found to be especially advantageous.<sup>1</sup>

The most obvious application for hardening resins is for the production of castings, for which purpose they are mixed with pigmenting or elastifying substances only; but their main application is as binders, adhesives, and impregnating agents, more especially for the production of electrical appliances. They are also used as varnishes, and so forth. There are also numerous other applications which can only be referred to briefly in the following description.

Finally, certain processes<sup>2</sup> for the solution or regeneration of hardened phenol-formaldehyde resins and waste are of interest.<sup>3</sup>

**Production of Castings.**<sup>4</sup> The first requirement for the production of castings is a supply of resole products which can be satisfactorily converted into resites, without any tendency to the formation of air-bubbles or cracks or subsequent shrinkage. These are usually produced by condensing crystallized phenol with an excess of formaldehyde, and evaporating the liquid primary resin so produced, in comparatively small batches, to a consistency which still just permits it to be poured into moulds. This is generally impossible without the addition of suitable substances such as glycerine.<sup>5</sup> Other additions may

<sup>1</sup> Bakelite Cor., U.S. Pat. 1,602,249; Canadian Pat. 265,674; British Pat. 275,011; French Pat. 620,144; Swiss Pat. 123,045; *C.* (1928), II, 295.

<sup>2</sup> Aylsworth, German Pat. 258,250 (1911); *C.* (1913), I, 1481; U.S. Pat. 1,027,794, 1,029,737; British Pat. 3,497-8 (1911); French Pat. 436,192; Heating with phenols or with phenols and naphthalene under pressure; C. Kulas, C. Pauling, German Pat. 412,170 (1923); *C.* (1925), II, 355; Gelatinization by heating with phenols; K. Albert and L. Berend, British Pat. 15,875 (1914); Austrian Pat. 84,475 (1916); *C.* (1921), IV, 714; German Pat. Application C, 30,325, Cl. 12q (21st June, 1921); Heating with considerable quantities of natural resins, such as colophony, or with cumarone resin, with or without the presence of acids or acid salts as accelerating catalysts; see also H. Bucherer, German Pat. 391,072; *C.* (1924), I, 2744; German Pat. 399,677; *C.* (1924), II, 1520; German Pat. 400,639; *C.* (1925), I, 309; German Pat. 456,820; *C.* (1928), I, 3002; Heating resites with natural resins and fatty acids of high molecular weight with formation of esters soluble in organic solvents, excepting alcohol.

<sup>3</sup> On the production of a porous resite which is easily subdivided, see Aylsworth, U.S. Pat. 1,092,512; *Kunstst.*, 4, 346 (1914).

<sup>4</sup> O. Gamber, *Die drechselbare Kunstharze*, Vienna and Leipzig (1926).

<sup>5</sup> On a method of operation with the use of a large amount of glycerine, see Carbaloid Products Cor., U.S. Pat. 1,668,445; *C.* (1928), II, 190.

also be made for obtaining special effects; these consist of colouring materials, or solutions of these in glycerine, phenol, and so forth, and also of products which improve the transparency of the ultimate products, or improve their properties as substitutes for ivory, tortoise-shell, and so forth, by the production of cloudy, turbid, opaque, and other effects. Thus, Story<sup>1</sup> claimed the production of opaque substances resembling ivory or bone by the addition of small amounts of fatty oils. The same effect is produced by small amounts of metallic salts. Similar effects are also produced by small amounts of turpentine oil, glycerine, vaseline,<sup>2</sup> phosphoric acid<sup>3</sup> (white translucent masses), and other substances.<sup>4</sup> Mottled coloured masses may be obtained by the addition to the product to be hardened of phenol-formaldehyde resin which has already been hardened and afterwards been subdivided.<sup>5</sup> Turbidity or a white coloration sometimes occurs in the course of the hardening process in consequence of the separation of finely distributed water.<sup>6</sup> Special effects can be produced by the addition of mica, bronze powder, or fish scales. It is also stated that pale colour, fastness to light,<sup>7</sup> and a better degree of transparency are attained by the addition of certain substances.<sup>8</sup>

<sup>1</sup> British Pat. 8,875 (1905); German Pat. 173,990.

<sup>2</sup> Van Voorhout, U.S. Pat. 1,271,392-3; French Pat. 483,417 (1917).

<sup>3</sup> Eilertsen, French Pat. 478,884 (1914); *Kunstst.*, 8, 46 (1918).

<sup>4</sup> On the addition of colloidal solutions which are themselves white or which separate white bodies on coagulation, such as thorium hydroxide, zirconium hydroxide or milk, see J. Kreidl, Austrian Pat. 98,387 (1922); *C.* (1925), I, 2262.

<sup>5</sup> Anglo-Oesterreichische Bank, Austrian Pat. 95,805 (1921); *Kunstst.*, 15, 184 (1925); *C.* (1925), I, 2472.

<sup>6</sup> In such cases the addition of citric acid has a favourable effect; see D. A. Spencer and H. D. Murray, *J. Soc. chem. Ind.*, 46, 637 (1927). On the effect of a highly specialized method, according to which the water is caused to separate in a highly dispersed form, the diameter of the drops being 0.3 to 0.5 $\mu$ , see F. Pollak, G.m.b.H., French Pat. 630,086; *C.* (1928), II, 815.

<sup>7</sup> Phosphoric and boric acids and their salts. Amalith Chem. Ind. G.m.b.H., L. Deutsch, J. Thorn, Swiss Pat. 107,627 (1923); British Pat. 207,792 (1923); French Pat. 573,150 (1923); *C.* (1925), II, 354.

<sup>8</sup> Aromatic carboxylic acid and their salts. Amalith Chem. Ind. Ges. m.b.H., L. Deutsch, J. Thorn, Swiss Pat. 107,628 (1923); British Pat. 207,791 (1923); French Pat. 573,148 (1923); *C.*, II, 354; on the addition of methylamines, see Rasan Kunstharzerz Ges.m.b.H., Austrian Pat. 102,677 (1921); *C.* (1926), II, 1476; J. Pollak, E. Möhring, U.S. Pat. 1,475,446 (1923); French Pat. 558,507 (1922); *C.* (1926), II, 1477; *Kunstst.*, 16, 254 (1926).

Otherwise, transparent products resembling amber are the most important; they can be obtained, of the desired amber shade, by hardening certain phenol-formaldehyde products which themselves possess the proper colour, but can also be produced in ruby, emerald, and other shades by colouring with aniline dyestuffs,<sup>1</sup> soot,<sup>2</sup> and so forth.<sup>3</sup> The colour of the phenols employed as raw materials is of considerable effect on the colour of the product, and this may lead to the necessity of distilling the phenols before use. Transparency is often ensured by the addition of small amounts of solvents.

The finished resole composition is poured into moulds of glass, metal, and so forth, whilst still warm,<sup>4</sup> and is then hardened by careful heating to 80–100° C. According to the patented process of Baekeland, the hardening process may also be carried out at higher temperatures by simultaneously applying pressure, in so-called Bakelisers (see Fig. 7), by which means the duration of the process is considerably decreased. The hardening process is accompanied by the difficulty that the products are easily discoloured through oxidation. When hardening in the bakeliser this disadvantage can easily be avoided by the use of inert gases.<sup>5</sup>

Many proposals have been made with regard to the character of the moulds,<sup>6</sup> especially for the production of hollow bodies. Thus, Pollak recommends the use of a hot mould,

<sup>1</sup> Story, German Pat. 173,900, proposed the addition of small amounts of naphthalene, tannic acid, and so forth.

<sup>2</sup> Story, German Pat. 173,990; pitch may also be used. According to D. A. Spencer and H. D. Murray, *J. Soc. chem. Ind.*, 46, 637 (1927), black colorations can with great advantage be produced by the addition of ammonium vanadate, or of a mixture of vanadium oxide and manganese dioxide.

<sup>3</sup> On a special method of coloration or of applying designs, see Rütgerswerke A. G., German Pat. 245,148; Austrian Pat. 52,507; *Kunstst.*, 2, 194 (1912).

<sup>4</sup> On forcing gelatinous masses into the moulds, see E. Redlhammer and Söhne, French Pat. 639,331; *C.* (1928), II, 2072.

<sup>5</sup> On storage of the finished products in containers filled with inert gases, see Redman, Weith, Brock, U.S. Pat. 1,345,695. Hardening in an inert atmosphere was also proposed by Story, German Pat. 173,990, as also hardening under oil; see also L. Deutsch, J. Thorn, and Amalith G.m.b.H., British Pat. 207,790.

<sup>6</sup> See also Bakelite Ges.m.b.H., German Pat. 441,022 (1925).

which revolves about its axis.<sup>1</sup> The proposal has also been made to form the cores of the moulds of low melting alloys,<sup>2</sup> or to form part of the mould of sulphur.<sup>3 4</sup> The interesting suggestion has also been made to mould by centrifugal force,<sup>5</sup> and also the use of moulds open at both ends in order that the moulded body may easily be removed.<sup>6</sup> On a special method of heating under pressure by means of heated or molten metals, see E. Novotny.<sup>7</sup>

Products built up of layers of varied colours can be produced by pouring and hardening the various layers separately.<sup>8</sup> Mottled effects can be produced by suitable mixing. Articles can also be produced which consist partly of synthetic resin, and partly of ebonite or other material.<sup>9</sup>

It is also stated that material free from air-bubbles can be obtained by compressing hardened phenol-formaldehyde resin powder or formaldehyde resin powder, which has previously been thoroughly dried for a prolonged period and so partially hardened.<sup>10 11</sup> It is questionable whether the mechanical properties of such masses would always prove satisfactory.

The hardened phenol-formaldehyde products, which are known as phenoplasts,<sup>12</sup> are sold under various names and in innumerable varieties. Products of this type are known as

<sup>1</sup> British Pat. 14,490 (1915); *Kunstst.*, 7, 69 (1917); 15, 44 (1925).

<sup>2</sup> Aylsworth, U.S. Pat. 1,135,962; *Kunstst.*, 9, 110 (1919); 14, 171 (1924); see also P. Pick, German Pat. 412,655 (1924); Resan A.-G., Austrian Pat. 108,680; *C.* (1928), I, 2016.

<sup>3</sup> R. Mannesmann, Swiss Pat. 79,992; *Kunstst.*, 14, 171 (1924); Austrian Pat. 86,229; *C.* (1922), II, 880.

<sup>4</sup> See also P. Pick, German Pat. 412,655 (1924); *C.* (1925), II, 356.

<sup>5</sup> Vickers, Ltd., N. E. Duffy, British Pat. 136,862; *Kunstst.*, 15, 44 (1925).

<sup>6</sup> Amalith Chem. Ind.-Ges. m.b.H., L. Deutsch, J. Thorn, German Pat. 412,189 (1923); *Kunstst.*, 15, 124 (1925); Austrian Pat. 97,787 (1922); Swiss Pat. 107,629 (1923); British Pat. 207,790 (1923); French Pat. 573,149 (1923); *C.* (1925), II, 355.

<sup>7</sup> U.S. Pat. 1,377,517; *Kunstst.*, 15, 42 (1925).

<sup>8</sup> Kabelfabrik und Drahtindustrie-A.-G., Austrian Pat. 94,216 (1921); *Kunstst.*, 15, 184 (1925); *C.* (1925), I, 2471; also M. Hilfreich, U.S. Pat. 1,668,590; *C.* (1928), II, 190; Kurz-Kasch Co., H. N. Copeland, British Pat. 259,252; *C.* (1928), II, 1499; Imitation wood.

<sup>9</sup> Dr. Heinrich Traun & Söhne, German Pat. 453,009; *C.* (1928), I, 978.

<sup>10</sup> E. Novotny, U.S. Pat. 1,398,149; *Kunstst.*, 15, 62 (1925).

<sup>11</sup> See Products Protection Cor., F. S. Smith, U.S. Pat. 1,586,850 (1920); *C.* (1926), II, 1207.

<sup>12</sup> O. Gamber, *Die drehelbaren Kunstharze*, Vienna-Leipzig (1926).

Bakelite C,<sup>1</sup> Juvelith,<sup>2</sup> Faturan,<sup>3</sup> Dekorite, Vigorite, Ambrasite, Amalith, Condensite, Resan, Redmanol, Herolith, Ornalith, Marbolith, Elastolith, and so forth, and in various colours, such as "amber,"<sup>4</sup> "ruby," "emerald," and so forth, and various other varieties, such as imitations of ivory, tortoise-shell, and horn. In addition, variously coloured, transparent, translucent, cloudy, opaque, uniformly coloured, banded or marbled masses are supplied for the various purposes of the fancy goods and turning industries. The products are marketed in the form of rods, plates, and so forth, of various dimensions, also as rough castings or mouldings, such as beakers, tubes, trays, vases, and so forth.<sup>5</sup>

Such plastic masses have a specific gravity of 1.22 to 1.30, a high dielectric constant, high refractive index,<sup>6</sup> and good mechanical properties.<sup>7</sup> The products show the exceptional resistance to chemical influences and to heat, described on page 331. Some of the materials become dielectric on being warmed or exposed to light, resembling amber in this respect. The better commercial qualities are also satisfactorily fast to light.

Observations on the elastic properties of phenoplasts have been made by O. Manfred and J. Obrist.<sup>8</sup> On page 338 are given the average values of the modulus of elasticity ( $E$ ), and of the maximum bending stress ( $S_{max}$ ), were obtained from a large number of individual determinations on a large number of

<sup>1</sup> See Baekeland, *Chem.-Ztg.* (1909), 317, 326, 347, 358; H. Lebach, *Chem.-Ztg.* (1913), 733.

<sup>2</sup> See *Kunstst.*, 8, 261 (1918); F. Pollak, *Chem.-Ztg.*, 37, 1233; *C.* (1913) II, 1782; *Chem.-Ztg.*, 45, 76 (1921).

<sup>3</sup> See *Kunstst.*, 4, 279 (1914); 7, 287 (1917); this contains analytical results.

<sup>4</sup> On the investigations of amber substitutes, see Marcusson, Winterfeld, *Mitt. Materialprüfungs-Amt.*, 30, 191; *C.* (1913), I, 68.

<sup>5</sup> C. Plonait, *Kunstst.*, 17, 275 (1927), gives specific gravities varying from 1.25 to 1.27; see F. Pollak, *Kunstst.*, 18, 61 (1928).

<sup>6</sup> According to C. Plonait, *C.* (1928), I, 2874, phenol-formaldehyde products show values of  $n_d$  varying from 1.650 to 1.662; natural amber shows a lesser value of  $n_d$ , varying between 1.5388 and 1.5451; on the transmission of light by Bakelite plates, see J. Risler, *Compt. rend.*, 181, 782 (1925); *C.* (1926), I, 1055; for infra-red rays, see Kimpflin, *idem*, 178, 1709; *C.* (1924), II, 584. Hardened papers were also tested.

<sup>7</sup> The elasticity is nearly equal to that of ebonite; the following breaking stresses were determined for Juvelith: compressional strength, 2,230 kg. per sq. cm.; tensile strength, 6 kg. per sq. cm.; bending strength, 250 kg. per sq. cm.

<sup>8</sup> *Kolloidtschr.*, 42, 174 (1927); *Angew.*, 41, 971 (1928).

commercial samples, bars and plates being dealt with separately. On detailed investigation it was found that the character of the specimens was by no means homogeneous, and that, for example, determinations made at various points of the same bar gave relatively large variations of the elastic modulus.<sup>1,2</sup>

		$E$ , kg. per sq. cm.	$S_{max}$ , kg. per sq. cm.
Bakelite	Bars	—	—
"	Plates	27,500	260
Juvelith	Bars	32,000	400
"	Plates	36,000	200
Dekorite	Bars	—	—
"	Plates	29,000	375
Vigorite	Bars	—	—
"	Plates	32,000	150
Ambrasite	Bars	34,000	—
"	Plates	—	150

The ease with which these products are worked, by boring, turning, grinding, carving, cutting, sawing, filing, and even by bending, and the high polish which they are able to take, have established them as valuable materials for the turning industry, and so forth. Their resistance to heat makes them particularly suitable for the production of smokers' requisites. They are also used for ornaments, such as beads, necklaces, brooches, and so forth; for buttons, stick and umbrella handles, stands, billiard balls, and writing requisites. (See summary on pages 362-4.) Phenoplasts are also used for objects exposed to special conditions, such as wheels which operate in the presence of oil or moisture, bottles and measuring cylinders for hydrofluoric acid, and so forth.<sup>3</sup> Products of exceptional moulding capacity have also been proposed for artificial dentures.<sup>4</sup>

<sup>1</sup> On the reason for this irregularity see O. Manfred and J. Obrist, *loc. cit.*; in this connection we refer the reader to the investigations of K. Haupt and M. Wächter, *Kunstst.*, 15, 129 (1915), and of O. Manfred and J. Obrist, *Angew.*, 39, 1293 (1926), which deal with the detection of internal strains, etc., of artificial horn products from casein by means of the irregular double refraction so produced.

<sup>2</sup> The balls show extraordinary elasticity, which is not impaired by climatic conditions; see H. Lebach, *Chem. Ztg.* (1913), 750.

<sup>3</sup> *Chem. Met. Eng.*, 33, 647 (1926).

<sup>4</sup> S. M. Kropman, Ph. Horowitz, British Pat. 261,447; C. (1928), II, 295; S. A. Wilding, Amalgamated Dental Co., Ltd., British Pat. 260,319; French Pat. 617,424; C. (1928), II, 295.

**Resoles as Binding Agents.** The hardening phenol-formaldehyde resins are largely used for the manufacture of press-mouldings, for which purpose they are mixed with various fillers, both of granular and fibrous character. Such press-mouldings are used as valuable electrical insulating materials, especially after the binder has been converted into the insoluble and infusible form.<sup>1</sup> Their hardness and resistance to heat and to chemicals, and especially to solvents, render them superior to

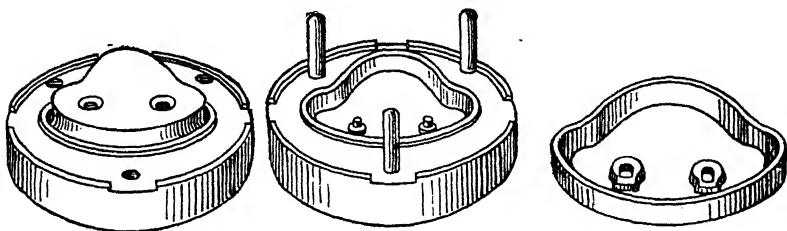


FIG. 8

many other materials, produced, for example, with bitumen, natural resins, and so forth.

Mixtures for press-moulding are prepared by intimately mixing or kneading the resoles with the fillers, either in finely-divided form, or in the form of a spirit solution. After any solvent has been removed by warming, preferably in vacuo, the dry mass, after powdering if necessary, is pressed in heated hydraulic presses at 160–170° C. at high pressure (about 150 kg. per sq. cm.) in heated moulds of hardened, polished steel. (See Fig. 8.) According to Baekeland's process,<sup>2</sup> both temperature and pressure are maintained unaltered until the hardening process is completed; this requires a few minutes only in the case of small and thin-walled objects, whilst for large, heavy and thick objects the time is correspondingly lengthened.

The combination of the moulding and hardening processes would lead to the occupation of the moulds for an impractically

<sup>1</sup> See also Urbanus, *Kunstst.*, 15, 189, 209 (1925); Stade, *Asphalt- und Teerindustrie-Ztg.*, 25, 826, 846, 865, 887, 925, 944 (1925); C. (1926), I, 1001; W. Demuth, *Elektrotechn. Zeitschr.*, 47, 1292 (1926); A. Bültemann, *Elektrische Isolierstoffe, insbesondere Bakelitmaterial*, Leipzig (1921).

<sup>2</sup> German Pat. 233,803 (1908); C. (1911), I, 1391; *Kunstst.*, 1, 215 (1911).



long time if resins were employed which hardened slowly, or if a low hardening temperature had to be employed on account of the nature of the filling material, for example, when sawdust is used as a filler. Occasionally, therefore, the hardening process is not entirely effected in the mould, in which it is allowed to proceed only until a condition of slight plasticity is attained whilst hot, after which the objects are completely hardened in the bakelizer in a suitable manner with slow rise of temperature. The temperature regulation must be even more careful if the final hardening is effected by heat alone, without pressure. According to another process the objects are merely moulded in the press whilst hot, and the actual hardening process is effected by subsequent heating at the ordinary pressure, with gradual rise of temperature until the process is completed.<sup>1</sup> The products so obtained are inferior to those hardened by simultaneous heat and pressure, as they do not show the same high polish, and have, therefore, to be subsequently varnished or polished in order to improve their appearance; for large objects, on the other hand, separate moulding and hardening offers advantages, as this procedure ensures that the objects are thoroughly hardened throughout, without the formation of an impermeable skin of resite, which may give rise to internal stresses in consequence of subsequent shrinkage.<sup>2</sup>

Other processes than those already mentioned have been proposed. Thus, E. Hemming<sup>3</sup> recommends cold moulding, using a mixture which contains liquid resole resins. The mouldings require exceptionally high pressures, but it is alleged that the dehydration, which necessarily precedes the actual hardening process, can be effected without impairing the soundness of the mouldings. After this drying operation, which must be effected at a suitable low temperature, the actual hardening of

<sup>1</sup> C. Kulas, C. Pauling, German Pat. 429,033 (1921); *Kunstst.* 16, 206 (1926); *O.* (1926), II, 657; French Pat. 547,450; *O.* (1923), IV, 541; British Pat. 203,733; *Kunstst.*, 15, 135 (1925); Redmanol-Gesellschaft, British Pat. 146,159.

<sup>2</sup> On the moulding of previously hardened material, see Baekeland, German Pat. 237,790 (1908); *Kunstst.*, 1, 437 (1911); U.S. Pat. 939,966; *Kunstst.*, 1, 216 (1910); U.S. Pat. 942,700, 1,259,472-3; Austrian Pat. 49,009; *Kunstst.*, 1, 417 (1911); Swiss Pat. 51,815-6; *Kunstst.*, 2, 77 (1912).

<sup>3</sup> U.S. Pat. 1,125,906 (1915); see also W. Petersen, E. V. Clark, British Pat. 179,586.

the binder is carried out by slowly raising the temperature, but at the ordinary pressure.

According to another process, mixtures of a dry and powdery character are press-moulded in the cold, with the addition of a dry lubricant, such as talc, soapstone, or similar material, immediately before moulding.<sup>1</sup> Resin products especially suitable for cold moulding have been described.<sup>2</sup> It certainly appears very questionable whether objects prepared in one way or another by cold moulding can be produced of the same high quality as those obtained by hot moulding and hardened with or without pressure.

The most important filler is wood meal, but fibrous and powdered materials, such as asbestos (for heat-resisting products),<sup>3</sup> china clay, graphite, ground wood, fibre dust, starch, paper pulp,<sup>4</sup> mica, fine sand, gypsum, slate powder, metal powders, and so forth, are also used.<sup>5</sup> Such materials are used partly for economy and partly because they endow the products with greater hardness, strength, elasticity, or other useful qualities.

<sup>1</sup> C. Kulas, C. Pauling, German Pat. 414,627 (1923); *C.* (1925), II, 1573; *Kunstst.*, 15, 165 (1925).

<sup>2</sup> C. Ellis, U.S. Pat. 1,645,693; *C.* (1928), II, 815; addition of wood oil or linseed oil with the fillers.

<sup>3</sup> Aylsworth, French Pat. 429,292; *Kunstst.*, 1, 437 (1911).

<sup>4</sup> Peabody, U.S. Pat. 1,083,755 (1914); Baekeland, U.S. Pat. 1,106,362; 1,160,365; *Kunstst.*, 6, 51, 62, 74 (1916); U.S. Pat. 1,213,144 (1917); Juchli, British Pat. 157,415 (1921); Weber, British Pat. 169,451; *C.* (1922), II, 345.

<sup>5</sup> In U.S. Pat. 942,699, Baekeland mentions the following fillers, which are copied from those used in the rubber industry: asbestos fibre, wood fibre, other fibrous or cellular materials, rubber, carbon, lamp black, mica, powdered minerals (such as zinc oxide, barium sulphate, etc.), pigments, dyestuffs, nitrocellulose, abrasives, lime, calcium, sulphate, graphite, Portland cement, powdered horn or bones, pumice, talc, starch, colophony, resins, gums, powdered slate, and so forth. The following have also been suggested: cellulose from corn cobs, Novotny, Kendall, U.S. Pat. 1,398,146; *C.* (1923), II, 754; hardened resite products, Aylsworth, U.S. Pat. 1,102,631 (1914); see British Pat. 6,405 (1912); *Kunstst.*, 3, 216, 417 (1913); masses resembling ivory and meerschaum can be obtained by adding a large proportion of magnesite, Römmeler, German Pat. 359,826 (1919); *C.* (1923), II, 340; *Kunstst.*, 13, 44, 57 (1923); hydrocellulose or oxycellulose: Petroff, German Pat. 380,596 (1921); *Färb.* XIV, 1142; *C.* (1923), IV, 962; British Pat. 231,431 (1925); *C.* (1925), II, 872; extract of lignite or peat: H. Plauson, German Pat. 376,743 (1914); *C.* (1924), I, 2849; powdered vulcanized fibre: Manfand, German Pat. 401,377 (1923); calcium carbonate, followed by lactic acid, to which sodium thiosulphate may be added: G. A. Lacroux, French Pat. 623,535; *C.* (1928), II, 294; ivory effects by the addition of lithopone, mottled effects with citric acid, and mother-of-pearl effects with calcium chloride; see 314 *et seq.*

They also counteract shrinkage and reduce internal strain. Obviously, the various fillings are of very varying effect in these respects, and special fillers or mixtures are therefore used for each purpose; moreover, various proportions have to be maintained between filler and binder, according to the circumstances.

According to Baekeland,<sup>1</sup> wood meal or fine sawdust is the best filler, but on account of its organic character it is somewhat sensitive to high temperatures, at which the dielectric properties are greatly reduced owing to its decomposition; moreover, it is not fire-proof. On the other hand, asbestos, which offers advantages over wood meal, being a heat-resistant filler, has also certain disadvantages. It is a comparatively poor insulator, and the strength and elasticity of the mouldings are not so high as when wood meal is used. Further disadvantages of the mouldings produced with asbestos are the rather high specific gravity, less satisfactory mechanical working properties (involving more wear of the tools) and comparatively poor lustre.

There is also a very definite difference between fibrous fillers and those of an amorphous or powdered character. The former only are capable of imparting to the phenol-formaldehyde products, which are hard and solid but comparatively inelastic, the required elasticity and pliability, which are necessary in order that the mouldings may withstand ordinary shock and bending stresses. Insulating press-mouldings ordinarily contain binder and both fibrous and powdered fillers; the fibrous material, such as asbestos, wood-pulp, cotton waste, wood meal, and so forth, is added to improve the elastic properties, whilst the non-fibrous filler serves to make the mass heavier or cheaper, and harder.<sup>2</sup> These general rules do not, of course, apply to masses containing resoles as binders only, but are of quite general application.

Greasy substances, such as oils or waxes, are also added to prevent the moulding from sticking in the mould;<sup>3</sup> the

<sup>1</sup> *Chem.-Ztg.* (1912), 1245.

<sup>2</sup> See Sommerfeld, *Angew.*, 40, 744 (1927).

<sup>3</sup> See Stokes, U.S. Pat. 1,557,318 (1923); *Kunstst.*, 16, 75 (1926); *C.* (1926), I, 1301; masses especially well suited, for cutting, boring, etc., are obtained by adding paraffin wax, mineral oil, and lanoline.

addition of 5 per cent of an organic carboxylic acid, such as lactic acid, has been recommended for the same purpose.<sup>1</sup> The inner surface of the mould may also be suitably treated, for example, with olein.<sup>2</sup>

We must now refer to various experiments in which the binder of resole character is mixed with substances which may themselves be considered either as binders or as fillers merely, such as bitumen,<sup>3</sup> pitches,<sup>4</sup> and more especially rubber or ebonite.<sup>5</sup> It is well known that by the addition of small amounts of hardening resins to bitumens or pitches the melting point of these materials can be greatly raised, and this fact is utilized for the production of press-mouldings.

For colouring the mass, black, brown or other coloured aniline dyestuffs are generally used, but sometimes pigments such as ivory black, iron oxides, or manganese dioxide.<sup>6</sup>

The fillers must be well mixed with the binder before pressing, and the latter must be able to flow to some extent in order thoroughly to impregnate the partially porous filler, as satisfactory mouldings can only be obtained in this

<sup>1</sup> Petersen, E. Clark, British Pat. 179,586 (1921); *C.* (1922), IV, 894; *Kunstst.*, 12, 165 (1922).

<sup>2</sup> On dusting with metallic soaps, see Ellis-Foster Co., H. M. Weber, U.S. Pat. 1,588,440 (1924); *C.* (1926), I, 1723; on dusting with hardening resin, in order to obtain especially lustrous surfaces, see Baekeland, U.S. Pat. 939,966; the mouldings may also be coated with resole varnish.

<sup>3</sup> L. Kirschbraun, British Pat. 188,012 (1921); *Kunstst.*, 14, 186 (1924).

<sup>4</sup> Favolle, French Pat. 341,013 (1904); Barringer, U.S. Pat. 1,091,621; *Kunstst.*, 4, 256 (1914); see also Cutler-Hammer Manuf. Co., U.S. Pat. 1,574,842 (1922); *C.* (1926), II, 113; Stearine pitch; Plausons Forschungsinst., German Pat. 354,539 (1919), acid tar, etc.

<sup>5</sup> Aylsworth, British Pat. 24,124 (1911); *Kunstst.*, 3, 96 (1913); 4, 98 (1914); French Pat. 435,944; U.S. Pat. 1,111,284 (1914); 1,092,511 (1914); Baekeland, U.S. Pat. 1,200,692 (1916); *Kunstst.*, 7, 68 (1917); Benjamin, U.S. Pat. 1,409,275-6-7 (1922); 1,493,062; Speedy, Crouch, British Pat. 171,803 (1920); *Kunstst.*, 13, 9 (1923); Wiechmann, U.S. Pat. 1,067,855-6 (1913) (other additions); *Kunstst.*, 3, 477 (1913); Grünwald, Austrian Pat. 83,275 (1915); *Kunstst.*, 12, 28 (1922); *C.* (1921), IV, 271; Felten & Guillaume Carlswerk A.-G., British Pat. 214,124; *Kunstst.*, 14, 187 (1924); Austrian Pat. 99,915; *Kunstst.*, 16, 159 (1926); Plausons Forschungsinstitut, German Pat. 378,003 (1921); *Kunstst.*, 14, 57 (1924); *C.* (1924), I, 2211; E. Gabriel, German Pat. 331,943 (1917), regenerated ebonite.

<sup>6</sup> On the addition of a diazo-compound, see Plauson and Vielle, British Pat. 182,497 (1921); *C.* (1923), II, 1032; U.S. Pat. 1,500,844; on the use of a triphenylmethane dyestuff, which is destroyed or changed at 150-200° C., and so indicates that hardening has occurred, see Pat.-Treuhand-Ges. f. elektr. Glühlampen m.b.H., German Pat. 385,125 (1922).

case.<sup>1</sup> This is easily effected by mixing and kneading machines if the binding agent is used as a liquid resin or spirit solution.<sup>2</sup> The mass so obtained is then dried, the solvent being volatilized in a vacuum and recovered. When using the ground solid resin the mixture must be kneaded in a heated mixer, a certain degree of care being necessary owing to the nature of hardening for resins. The mass is then introduced into the moulds in the form of powder or of strands, and moulded as already described. The material is frequently pre-formed into tablets (see Fig. 9),

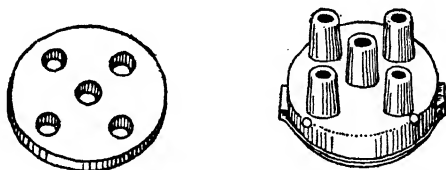


FIG. 9

which are produced by a preliminary compression. This procedure offers the advantage that the quantity of material necessary to fill the mould does not need to be weighed each time, but is supplied automatically. Regarding details of the tabulating process, we must refer the reader to the descriptions by C. Ellis, W. Demuth, Sommerfeld, and others.<sup>3</sup> We will only mention that the most complicated objects can be moulded, provided with perforations, bars, and threads, and with inserts of metal, rubber, or other materials. Very great precision is attainable, both in the moulding and in the position of the

<sup>1</sup> On the importance of prolonged mixing, see O. Manfred, J. Obrist, *Kolloid-Ztschr.*, 41, 348 (1927); *Angew.*, 41, 971 (1928).

<sup>2</sup> On water as a liquid medium, see Baekeland, Austrian Pat. 52,291; *Kunstst.*, 2, 213 (1912); U.S. Pat. 1,160,362 (aqueous alkalies); Grünwald, German Pat. 339,426 (1917); French Pat. 517,832 (1919); *C.* (1921), IV, 196; Swiss Pat. 75,776; *Kunstst.*, 8, 306 (1918); Czechoslov. Pat. 12,341; *Kunstst.*, 16, 207 (1926); Condensite Co., U.S. Pat. 1,146,299; 1,146,300; *Kunstst.*, 6, 110 (1916); alkaline solution; G. Petroff, German Pat. 379,983 (1922); *Frdl. XIV*, 705.

<sup>3</sup> C. Ellis, *Synthetic Resins and Their Plastics*, pp. 358-459; W. Demuth, *Elektrotechn. Ztschr.*, 47, 1292; Sommerfeld, *Angew.*, 40, 744 (1927); the principles on which insulating mouldings should be designed have been indicated by Siemens-Schuckert-Werke; see also O. Fischer, *Elektrotechn. Ztschr.* (1923), Part 52; Urbanus, *Kunstst.*, 15, 189, 209 (1925); C. H. Bryson, *Kunstst.*, 17, 134, 180, 230 (1927); A. Sommerfeld, *Gummifreie Isolierstoffe*, Berlin (1927); *Elektrotechn. Zeitschr.* 48, 1622 (1927).

inserts.<sup>1</sup> It is also of importance that the moulding can be united with objects of other composition during the moulding process.<sup>2</sup>

Numerous important articles for the electrical industry are produced in the manner indicated above, which are much used, for example, for current supply and distribution, such as insulators, insulating stands, covers, switchboards, end caps for cables, coil bobbins, distribution discs, brush holders for dynamos, switch boxes, radio parts, and so forth. Other articles which are similarly produced are motor-car parts (such as handle, steering wheels, door-handles, lighting switches, connection plugs, gear wheels, and also knife handles, bobbins (for electrical and other purposes), handles (for hot irons, crucibles, knives, brushes, hand mirrors, and so forth), pegs, plates, furniture castors, buttons, acid-proof cocks, medical instruments, and so forth. (See list, pages 364-4.) Attempts have been made to construct gramophone discs of hardening phenol-formaldehyde resins,<sup>3</sup> but so far it has been found impossible to displace natural shellac from its predominant position for this purpose. The resoles have, however, attained great importance for the production of emery wheels and other grinding wheels.<sup>4</sup> It has also been found possible, by the use of suitable fillers which conduct heat well, such as graphite and metals,

<sup>1</sup> On the other hand, on burning porcelain the shrinkage is 6 to 8%, and 10% on burning steatite; Günther-Schulze, *Angew.*, 40, 788 (1927). Lead borate behaves in a more satisfactory manner and is used as an insulator, more especially after mixing with finely divided mica, as "Micalax," which is now much used for high frequency radio installations; see Guy Bartlett, *C.* (1927), II, 154.

<sup>2</sup> The figures have been kindly placed at our disposal by the Bakelite Corporation, New York, and are to be found in their pamphlet "Bakelite Moulded," which gives a very instructive description of the method of moulding bakelite. The presses which are required are partly of specialized construction, and are constructed, in Germany, by the following firms among others: "Wumag," Görlitz; J. L. Hütten, Düsseldorf; J. Banning, Hamm i.W. On a heating press with cooling contrivance, see E. P. Darragon, French Pat. 639,249; *C.* (1928), II, 2072.

<sup>3</sup> Baekeland, U.S. Pat. 1,083,264 (1913); Aylsworth, U.S. Pat. 1,060,577; 1,061,258; 1,092,512; 1,071,685; 1,110,417; 1,146,384-5-6-7-9; 1,146,390-1; 1,151,849; 1,167,468; 1,170,391; 1,230,816; 1,255,500; 1,283,450; Edison, U.S. Pat. 1,146,413; Beatty, U.S. Pat. 1,158,964; Römmler, British Pat. 174,372 (1922); Gesellschaft für hygienische Erzeugnisse G.m.b.H., French Pat. 593,897 (1925); *C.* (1926), II, 1594.

<sup>4</sup> Baekeland, U.S. Pat. 942,808 (1909); Aylsworth, U.S. Pat. 1,090,440 (1914); *C.* Krug, German Pat. 410,412 (1922).

to produce antifriction compositions.<sup>1</sup> Further products which are so obtained are safety steps,<sup>2</sup> brake linings,<sup>3</sup> certain electric apparatus,<sup>4</sup> fireproof articles,<sup>5</sup> wood substitutes,<sup>6</sup> packing agents (such as resistant packings for stuffing boxes, packing rings for pistons, and so forth),<sup>7</sup> transformer cases for electric machinery,<sup>8</sup> pistons,<sup>9</sup> and so forth.<sup>10</sup> partly of special design. They are also used for heaters of various kinds, resistant to chemicals,<sup>11</sup> filter-press plates,<sup>12</sup> porous filtering masses,<sup>13</sup> heat-insulating compositions (with cork),<sup>14</sup> and, finally, for the construction of chemical plant of "Haveg" composition, which is exceptionally resistant, especially to hydrochloric acid, salt solutions, hydrofluoric acid,<sup>15</sup> etc., and is also highly resistant to sudden temperature changes; this composition is of great mechanical strength and easily repaired.<sup>16</sup> Attempts have also been made to use hardening phenol-formaldehyde resins as matrices for printing.<sup>17</sup>

<sup>1</sup> Baekeland, German Pat. 226,887 (1909); *C.* (1910), II, 1350; *Kunstst.*, 1, 56, 171 (1911); U.S. Pat. 941,605.

<sup>2</sup> Hopp, U.S. Pat. 1,156,081 (1915); *Kunstst.*, 9, 150 (1919).

<sup>3</sup> The Raybestos Co., U.S. Pat. 1,498,386 (1921); *C.* (1925), I, 2473; *Kunstst.*, 15, 181 (1925); U.S. Pat. 1,519,322; *C.* (1928), II, 2464; Ferodo, Ltd., German Pat. 413,863 (1920); see also British Pat. 12,881 (1917); 15,565 (1917); 4,051 (1918); Rathnow, Trietschler, German Pat. 373,613; Kirchbachsche Werke Kirchbach & Co., Swiss Pat. 124,122; *C.* (1928), II, 1723.

<sup>4</sup> P. Hebert, French Pat. 603,621; *C.* (1926), II, 657; *Kunstst.*, 16, 231 (1926).

<sup>5</sup> F. B. Daneshower, U.S. Pat. 1,450,140; *C.* (1923), IV, 139.

<sup>6</sup> Esgam, German Pat. 402,707 (1921); *C.* (1924), II, 2439; *Kunstst.*, 15, 123 (1925).

<sup>7</sup> Baekeland, German Pat. 223,714 (1909); Austrian Pat. 52,291; U.S. Pat. 942,808; 942,852; 942,858; Swiss Pat. 45,529; 54,511; French Pat. 11,628, addition to 386,627; *Kunstst.*, 1, 171 (1911).

<sup>8</sup> R. A. L. Volet, German Pat. 397,518 (1920).

<sup>9</sup> Ch. de Lucacsevs, E. Löffler, U.S. Pat. 1,398,178, 1,407,667 (with mica flakes and metallic insert); W. Hack, U.S. Pat. 1,486,110 (Fibre as filler).

<sup>10</sup> Baekeland, U.S. Pat. 1,054,265 (1913); Kempton, U.S. Pat. 1,392,173-4 (1922).

<sup>11</sup> Säureschutz-Ges. m.b.H., J. K. Wirth, German Pat. 420,338 (1924); *C.* (1926), I, 748. "Haveg"-Material.

<sup>12</sup> Säureschutz-Ges. m.b.H., German Pat. 401,376 (1923); *Kunstst.*, 15, 28 (1925); *C.* (1924), II, 2429. Production of furrows by grinding.

<sup>13</sup> Säureschutz-Ges. m.b.H., German Pat. 421,512 (1924).

<sup>14</sup> French Pat. 637,721; *C.* (1928), II, 1805.

<sup>15</sup> On an apparatus of transparent Bavelite for measuring hydrofluoric acid, see Curtmann, *J. Ind. Eng. Chem.*, 14, 610; *C.* (1922), IV, 605.

<sup>16</sup> J. K. Wirth, *Chem.-Ztg.*, 49, 653 (1925); 51, 349 (1927); H. Lebach, *Angew.* 38, 1091 (1925).

<sup>17</sup> Aylsworth, German Pat. 290,574; *Kunstst.*, 6, 135 (1916); U.S. Pat. 1,098,610 (1914); 1, 144,338 (1915); Baekeland, U.S. Pat. 1,233,298 (1917);

The press-mouldings obtained with hardening phenol-formaldehyde resins as binders, known commercially under the names of Bakelite, Bosch-bakelite, Bakdura, Durax, Estralite, Ambroin, Ricolite, "Isolierstahl," Gummon, Redmanol, Condensite, Trolon, Trolite, Tenalan, Tenacite, and so forth, possess good mechanical, chemical and physical properties. Thus, they are exceptionally good insulators, and numerous measurements and observations on this property are to be found in the literature.<sup>1</sup> We here merely append a table which was published in the Technologic papers of the Bureau of Standards, No. 216. This is all the more of interest as the properties of ordinary bakelite mouldings are compared with a laminated bakelite product, with ebonite and with vulcanized fibre.

**Resoles as Impregnating Agents and Adhesives.** Apart from press-mouldings, laminated materials play an important and indispensable part as electrical insulators, etc. These products are prepared<sup>2</sup> by coating webs of paper and so forth with suitable binders,<sup>3</sup>

German Pat. 320,180 (1913); *C.* (1920), IV, 135; Redman, Weith, Brock, *J. Ind. Eng. Chem.*, 9, 388 (1917); *C.* (1918), I 317; Williamson, German Pat. 271,898 (1913); *C.* (1914) I, 1386; U.S. Pat. 1,173,907 (1916); Yeoell, U.S. Pat. 1,379,430-1-2-3-4 (1922); Stokes, German Pat. 346,950; *C.* (1922), II, 1112; Novotny, Kendall, U.S. Pat. 1,398,146; *C.* (1923), II, 754; paper is often used as a filler, which is impregnated by the binder.

<sup>1</sup> See, for example, F. W. Hinrichsen, "Ueber Isoliermaterialien der Elektrotechnik und ihre Prüfung," *Kunstst.*, 4, 41, 64 (1914), which contains exact methods and directions; Bültemann, *Kunstst.*, 7, 292 (1917); 12, 66, 76, 82 (1922); Vosmaer, *Chem. Weekblad*, 17, 36; *C.* (1920), II, 646; see also *Kunstst.*, 12, 113 (1912), on British testing methods; also O. Fischer, *Elektrochem. Ztschr.* (1923), Part 52; on the regulations of the V.D.E. for testing insulating materials, see also *Vorschriftenbuch des V.D.E.* (Springer, 1926), and also the Appendix to this book. See also W. Demuth, *Die Materialprüfung der Isolierstoffe der Elektrotechn. Ztschr.* (1927), 539. Further details and results of tests are to be found in innumerable scattered publications and small monographs. We must also mention U. Retzow, *Eigenschaften elektrotechn. Isoliermaterialien in graphischen Darstellungen*, Berlin (1927); A. Sommerfeld, *Gummifreie Isolierstoffe*, Berlin (1927); *Elektrotechn. Zeitschr.*, 48, 1622 (1927); H. Stäger, *Kolloidchemie der Isoliermaterialien* ("Kolloidchemische Technologie," Dresden-Leipzig, 1926, p. 264 *et seq.*); C. H. Bryson, *Kunstst.*, 17, 134, 180, 230 (1927); J. Simonin, *Rev. gén. Matières plast.*, 3, 687 (1927); A. Bréguet, *Rev. gén. Colloides*, 5, 681 (1927); W. Nagel, *Angew.*, 41, 685 (1928); A. A. Drummond, *Chem. Trade Journ.*, 82, 5 (1928); *India Rubber Journ.*, 75, 101 (1928); J. Obrist, *Kolloid-Zeitschr.*, 45, 82 (1928), etc.

<sup>2</sup> See Bültemann, *Kunstst.*, 12, 76 (1922); K. J. Breuer, *Kunstst.*, 15, 34 (1925); see also Bültemann, *Kunstst.*, 9, 49, 65, 91 (1919), who also shows figures of some of the products.

<sup>3</sup> Coating machines and machines for the production of wound articles, and so forth, are built by the following firms, amongst others: Keller & Prahl, Eschwege a.d. Werra and E. Jagenberg, Düsseldorf.



# COMPARISON OF PROPERTIES OF HARD RUBBER, VULCANIZED FIBRE, LAMINATED AND MOULDED PHENOLIC INSULATING MATERIALS

Properties	Hard Rubber	Vulcanized Fibre	Phenolic Insulating Materials	
			Laminated	Moulded
Surface resistivity at 50% relative humidity, ohms.-inches	$10^{12}$ to $10^{15}$	—	$10^{11}$	$10^{11}$
Phase difference ( $Z$ ) at radio frequencies, degrees	0.5*	8.0†	1.5 to 4.0	1.5 to 4.0
Dielectric constant ( $K$ ) at radio frequencies	3.0*	5.0†	4.5 to 6.0	5.0 to 7.5
Dielectric strength . . . volts per mm.	10,000 to 38,000†	9,000 to 16,000 ††	27,000 to 45,000†	9,000 to 40,000††
Tensile strength . . . lb. per in. <sup>2</sup>	3,500 to 6,500	6,000 to 20,000	10,000 to 25,000	3,500 to 7,000
Water absorbed in 24 hours, percentage by weight	0.02	26 to 45*	0.2 to 1.0†	0.05 to 0.20
Density . . . g. per cm. <sup>3</sup>	1.12 to 1.40**	1.3 to 1.5	1.3 to 1.4	1.3 to 1.4
Thermal expansivity (at 20 to 60° C.)	60 to 80 × 10 <sup>-6</sup>	27 × 10 <sup>-6</sup>	20 to 30 × 10 <sup>-6</sup>	25 to 45 × 10 <sup>-6</sup>
Effect of age	Deteriorates slowly, but if properly vulcanized and protected from the light it is not affected	Improves in quality by seasoning**	Improves*	No deterioration in physical or chemical properties; slight increase in hardness††
Heat	At 65-75° C. (150° F.) pure hard rubber softens perceptibly; at 106° C. (222° F.) it is so soft it may be bent easily; at 115-5° C. (240° F.) it becomes leathery and may readily be cut with a knife; melts at 200° C. (382° F.)**	Will not melt under any circumstances; not readily inflammable; at very high temperature chars and becomes brittle; active composition begins at about 343° C. (650° F.)	Not readily inflammable; will withstand continuously a temperature of 149° C. (300° F.); heat tends to complete the reaction and volatile substances are driven off. Hence, when cooled it shrinks considerably and may split; shrinks and loses in weight above 80° C.††	See statement for laminated materials††
Smight	Discolours and disintegrates after a few months; the surface of the hard rubber is oxidized, forming the equivalent of sulphuric acid; this may take up ammonia from the air or may attack the lining materials forming the various supplies upon the surface; the surface resistivity is greatly reduced.**	No effect‡	No visible effect**	After 2½ years some materials show a slight change, such as discoloration or very fine cracks; other materials shown no such change*

Effect of ultra-violet light  
for 20 hours

Discoloration and slight brittleness. The rubber, as pronounced for a few hours' exposure to ultra-violet light as for many months exposure to sunlight; the surface resistivity is greatly reduced.\*\*

No data . . .

Appreciable lowering of surface resistivity

Appreciable lowering of surface resistivity.\*\*

Moist air . . .

Hard rubber compounds excepting those containing organic substances other than rubber are practically moisture proof.

The only effect is that due to the high temperature

Absorbs water freely, but without permanent injury; while saturated it becomes soft and flexible and swells; warps and twists upon drying as above, except absorption is more rapid

Absorbs slight amount of water, reducing dielectric properties†

Absorbs slight amount of water, reducing dielectric properties

Steam . . .

The only effect is that due to the high temperature

The only effect is that due to the high temperature

Best grades not affected by steam; after a few days in steam the cheaper grades will swell appreciably and split; superheated steam tends to warp and blister all grades of the material

Absorbs a slight amount of moisture; if steam is superheated, the high temperature will cause decomposition

Absorbs a slight amount of moisture; if steam is superheated, the high temperature will cause decomposition

Solvents—

Acetone . . .

Attacks, dissolving oils and free sulphur\*

No permanent effect\*

No effect\*†

No effect\*†

Alcohol . . .

Attacks to a slight degree\*

No permanent effect\*

No effect\*†

No effect\*†

Ammonia . . .

No effect\*

No permanent effect\*

No effect\*†

No effect\*†

Aniline . . .

Softens it at ordinary temperature\*

Not known . . .

No effect\*†

No effect\*†

\* These values were obtained at frequencies between 750,000 and 75,000 cycles per second (300 to 4,000 metres wave length), there being very little change throughout this range. The grade of the sample tested is unknown, so values differing somewhat from these might be expected on other samples using different quantities and kinds of filler.

† Values of  $\gamma$  and  $K$  may be somewhat lower or much higher, depending on amount of moisture present in the filler.

\*\* Information obtained from sources other than the Bureau of Standards.

under which tests are made.

†† The Railway Signal Association specifications require an absorption when immersed in water at 70° F. for 24 hours, not to exceed 15% by weight for 1 lb. filler, 30% for 1 in. filler, 40% for 1 in. filler.

‡‡ Dependent upon nature of sample, size, surface area, and kind and amount of filler.

§§ Values with reference to the amount of sulphur present and increases with the increase in amount of filler. Pure hard rubber ranges from 1-12 to 1-25.

|| The density of several quality rubbers from 1-25 to 1-40.

¶ This means seasoning or ageing in a protected place, such as a storage house.

‡‡ These materials are of comparatively recent development, and hence no information has been gained covering very long periods. Theoretically, under certain conditions the chemical reactions would tend to continue, which would age and improve the material. The manufacturer claims a slight improvement in dielectric properties and a marked improvement in machining qualities when the ageing takes place under ordinary atmospheric and temperature conditions. If the ageing takes place in a moist atmosphere, the dielectric properties are subject to deterioration.

COMPARISON OF PROPERTIES OF HARD RUBBER, VULCANIZED RUBBER, LAMINATED AND MOULDED PHENOLIC INSULATING MATERIALS—Continued

Properties	Hard Rubber	Vulcanized Rubber	Phenolic Insulating Materials	
			Laminated	Moulded
Solvents (continued)—				
Benzol . . . . .	Softens it at ordinary temperature*	No permanent effect*	Probably no effect†	Probably no effect†
Carbon bisulphide . . . . .	Dissolves small amount of hard rubber and any free sulphur	No permanent effect*	Probably no effect†	Probably no effect†
Ether . . . . .	Dissolves small amount of hard rubber and any free sulphur	No permanent effect†	No effect†	Probably no effect*
Naphtha . . . . .	Softens and swells to slight extent†	No permanent effect†	Probably no effect†	Probably no effect†
Oil of turpentine . . . . .	Dissolves in boiling oil†	No permanent effect†	Probably no effect†	Probably no effect*
Oil—				
Mineral . . . . .	Slight softening†	Slight absorption†	Practically impervious†	Practically impervious†
Organic . . . . .	Unaffected†	Swells, due to absorbed water; may be attacked after some time†	Practically unaffected except for absorption of water*	Practically impervious†
Effect of weak acids . . . . .	Unaffected†			Practically unaffected†
350 Weak caustic alkalis . . . . .	Unaffected . . . . .	Swells, due to absorbed water; may be attacked after some time†	Does not successfully resist the action of alkali unless very dilute	Does not successfully resist the action of alkali unless very dilute
Stronger acids (HNO <sub>3</sub> , HCl, H <sub>2</sub> SO <sub>4</sub> ) . . . . .	Not attacked by concentrated hydrochloric, hydrofluoric, acetic acids; not attacked by sulphuric acid of less than 1.50 specific gravity or nitric acid of less than 1.12 specific gravity†	Cellose fibre attacked soon decomposes	Does not successfully resist the action of alkali unless very dilute	Decomposes; rapidly depends on specific gravity and temperature of acid
Stronger caustic alkalis . . . . .	No effect . . . . .	Cellose fibre attacked soon decomposes	Binder and filler decompose*	Completely destroyed; speed of the reaction depends on the strength of the solution
Ozone . . . . .	Oxidizes and soon ruins it for electrical purposes	No effect†	Not known . . . . .	Not known
Metallic inserts . . . . .	Rapidly deteriorated by contact with iron or copper, the metals themselves being corroded; the inserts should be coated with tin, paper, vulcanized rubber, or other mutually protecting medium	No effect . . . . .	No effect . . . . .	No effect

# Machining qualities

Cost	Admits of a high polish; machines less accurately than would be supposed, due to great resistance; the better the grade the more readily it is machined; quality may be judged roughly by colour and texture, toughness, colour, and grain of a slaving; has tendency to warp; can be moulded but not accurately to size	Admits of a fine finish; may be sawed, punched, drilled, stamped, embossed, turned, planed, joint, tapped (rough); resists shock; cannot be moulded††	Admits of a good polish; can be sawed, punched, drilled, stamped, turned, planed, knurled, embossed, milled, tapped either with or against the grain, though not so easily as hard rubber and vulcanized fibre; tough; resists shock; cannot be moulded†	Admits of a fine finishing polish; can be machined, cut, filed, sawed with difficulty; can be moulded accurately to size; quite brittle
Cost	About \$2 per lb. in sheet form	50-80 reols per lb. up to 1 in. in thickness; about \$2 per lb. for 2 in. in thickness	About \$1 per lb.	Cost varies with complexity of sized moulds

331

- \*+ See pp. 580-583 and 187 of this paper.
- \*\* When subjected to temperatures above 60° C. (140° F.) some of the volatile matter is driven off, resulting in the shrinking and loss in weight of the material. This can be carried out many times with the same result, the material becoming more brittle. Tests made on these materials show that they are very erratic in behaviour and do not expand or contract in a uniform way. It seems altogether probable that a joint would be reached after all volatile matters had been driven off, when further subjecting to a moderate temperature and subsequent cooling would not result in further shrinkage. This has not been proved experimentally. High temperature will produce decomposition. Further information regarding these tests will be found in Scientific Paper of the Bureau of Standards No. 352. (See also pp. 580-583 and 187 of this paper.)
- †† A further discussion of the tests at the Bureau of Standards may be found in Scientific Paper of the Bureau of Standards, No. 231.
- † See effect of ultra-violet light.
- †† See discussion on pp. 589 and 600 of this paper.
- †† Strong solvents affect the phenolic binder of the sheet material too brittle for general use. When water is present, the material will absorb it in various amounts.
- †† Information obtained from sources other than the Bureau of Standards.
- †† Strong solvents affect the phenolic binder of the material to a limited extent unless the chemical reaction has been carried to the point where it is in the insoluble state. This condition would render the sheet material too brittle for general use. When water is present, the material will absorb it in various amounts.
- †† The effects vary with the materials, different moulding mixtures, and acids. Nitric acid is harmful. In general, weak acids will mar the surface and attack the edges of a sample soon after it comes in contact with the sample, but there is little or no further damage.
- †† See 1. 608 of this paper.
- †† The action differs for various materials and grades. Some materials resist the action of a 30% solution of H<sub>2</sub>SO<sub>4</sub> for several months and will withstand hydrochloric acid without any visible signs of attack. On other materials of this class sulphuric and nitric acids attack the surface of the sample and form a protective coating. This makes the sample as far as further electrical use is concerned, but on removing the sample from the acid and cutting it open it is found that the acid has not penetrated more than 1/16 in. after several months exposure to the acid.
- †† Thin sheets can be pressed to simple shapes when warm.

and then uniting a suitable number of layers under the influence of heat and pressure. The only natural product used as a binder is shellac, which is equalled or even exceeded in the necessary good qualities by the resoles only. Other artificial resins play a quite subordinate part, and are only used in special cases. (See page 203, 268.)

The demand for laminated products in the form of plates, blocks, tubes of very various wall thickness and diameter, up to more than one metre, and of other hollow bodies, is enormous; the structural element is usually paper, which is impregnated by machinery in the form of sheets or webs, with a solution of resole resin in spirit, then dried, sometimes in a current of warm air with recovery of the solvent, and then stacked.

In order to produce plates, the required number of varnished sheets are piled and the last one covered with an unvarnished sheet. The bundle is then placed in a heated hydraulic press, in which it is submitted to high pressure and simultaneously heated. This first causes the resin to become fluid, so that the sheets are intimately united without any interspaces. This process is followed by that of the transformation of the resin, by which the whole mass is welded to a single plate of exceptional mechanical and electrical properties. (See page 347 *et seq.*) The thickness of the plates may be varied within fairly wide limits. Quite thin sheets can be produced, and also blocks of 10 cm. thickness and over. The other dimensions, obviously, depend on the size of the sheets of paper.<sup>1</sup> Smaller sizes are cut out of larger plates.

For the production of tubes and other hollow bodies special winding machines are used. (See Figs. 10 to 13.)<sup>2</sup> In these a coated paper web is first passed over a heated roller, by which the binder is melted, and then passes immediately on to a mandril which reproduces the internal shape of the article to

<sup>1</sup> On the union of laminated plates edgewise, in order to obtain larger sizes, see Bakelite-Ges. and H. Lebach, German Pat. 375,439 and 388,150.

<sup>2</sup> Fig. 10 is taken from the article by H. Stäger on "Synthetic Resins" in *Kolloidchem. Technologie*, Dresden and Leipzig (1927), p. 297. Figs. 11-13 have been kindly placed at our disposal by A. G. Brown, Boveri & Co., and the affiliated company Micafil-A.G.

be produced. (See Figs. 10 and 13.) The wall-thickness of the product depends entirely on the number of turns of the winding. It is important that the paper should be maintained at the correct tension; the binder is prevented from solidifying prematurely by the action of auxiliary heating rollers, which also exercise the function of ensuring that the several layers are tightly folded and united without any discontinuities. After the required thickness has been attained, the mandril and sur-

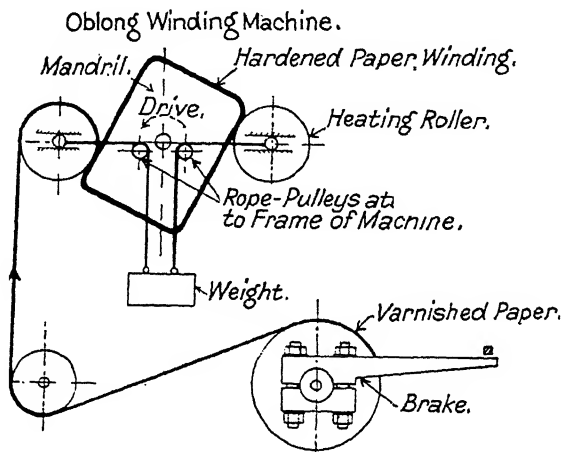


FIG. 10. DIAGRAM OF A WINDING MACHINE

rounding wound object are removed from the machine together, and placed in a stove in which the gradual transformation of the binder is effected at a moderate temperature of 80–90° C. The quality of the article depends greatly on the proper conduct of this operation, so that the correct degree of hardening may be produced without the formation of blisters between the numerous layers.<sup>1</sup> The break-down resistance of the products is also greatly dependent on the absorptive capacity of the paper which is employed.<sup>2</sup> It should be noted that the

<sup>1</sup> See also Frederick, U.S. Pat. 1,284,295–6–7–8–9 (1918); Kempton, U.S. Pat. 1,284,363 (1918); Burningham, Richter, van Arshed, White, U.S. Pat. 1,396,021 (1921); Trombert, French Pat. 590,756 (1924); C. (1926), I, 273; *Kunstst.*, 16, 76 (1926); H. Stäger, *Kolloid-Zeitschr.*, 46, 66 (1928).

<sup>2</sup> Breuer, *Kunstst.*, 15, 17 (1925).

electrical breakdown resistance along the length of the winding is only about one tenth of that across it.<sup>1</sup>

Numerous proposals have been made for the production of such laminated material,<sup>2</sup> dealing, not only with the mechanical

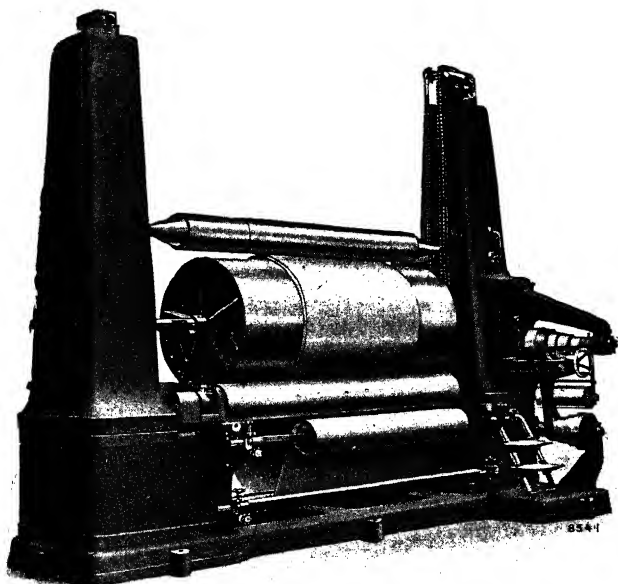


FIG 11.

arrangements, but also with the use of fabrics other than paper, such as fibre, linen, and cotton cloth, asbestos and mica flakes

<sup>1</sup> Schwenkhagen, *Elektrizitätswirtschaft*, 26, 342 (1927).

<sup>2</sup> Baekeland, U.S. Pat. 1,019,406 (1912); Frederick, U.S. Pat. 1,284,644 (1918); McIntosh, U.S. Pat. 1,236,460 (1917); O'Connor, U.S. Pat. 1,284,432 (1918); Stevenson, U.S. Pat. 1,295,230 (1919); Wright, U.S. Pat. 1,303,753 (1919); J. Gebhard, German Pat. 326,783 (1919); Vulkanfiber; Stevenson, U.S. Pat. 1,392,535 (1921); Taylor, U.S. Pat. 1,441,133 (1923); Metropolitan-Vickers Electrical Co., Ltd., British Pat. 169,451 (1921); Kempton, U.S. Pat. 1,309,758, 1,312,789 (1919); 1,416,036 (1922); Egerton, U.S. Pat. 1,370,800 (1921); Frederick, U.S. Pat. 1,430,541 (1922); Bakelite Cor., K. Brown, U.S. Pat. 1,559,846 (1923); *C.* (1926), I, 1740; Westinghouse Electric & Manuf. Co., U.S. Pat. 1,448,386; Comp. Franç. pour l'Exploitation des Procédés Thomson-Houston, French Pat. 602,428 (1924); *C.* (1926), II, 476.

(micanite), and so forth, and also with various other modifications.<sup>1</sup> The fault which sometimes occurs through distortion of the material is stated to be remedied by a short heating to 170–200° C. and immediate cooling, these operations being repeated several times if necessary. The manufacture of these products requires considerable practical experience.

Laminated insulating articles are sold under various names, such as the following hardened papers: Presszell, Geax, Bikarton, Bituba, Bakelite paper, Carta, Durax, Turbonite, Turax,

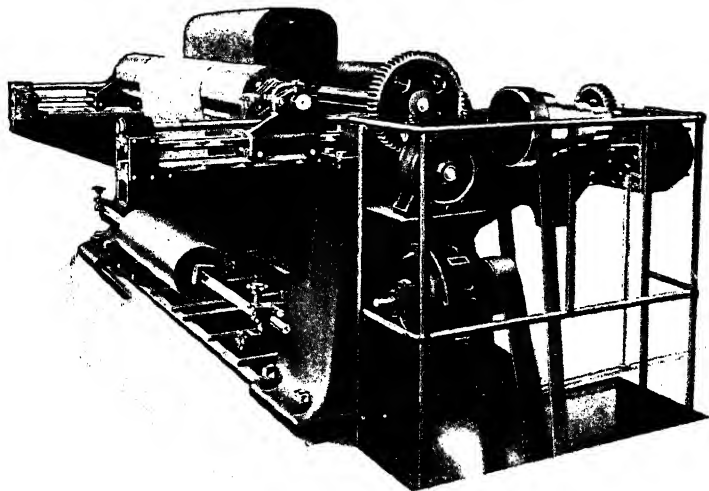


FIG. 12

Pertinax, Neolite, Harex, Repetite, Peralite, and so forth; hardened fabrics: Novotext, Turbax, Pertinax, Harex, and so forth; Mica products, or Micanite: Press Micanite, Megohmite, Mikarta, Mikafolium, Mica paper, Mica fabric, Mica asbestos, etc.<sup>2</sup> On the properties of the materials, see the table on page 348 *et seq.* and the cited investigations.<sup>3</sup> Materials of this character are easily worked mechanically, and are widely

<sup>1</sup> On dusting resin powder between paper webs, instead of application in varnish form, see Emil Haefely & Cie, A.-G., German Pat. 323,599 (1918).

<sup>2</sup> On Canevasite plates, for example, see *Kunstst.*, 13, 81 (1923).

<sup>3</sup> See also Retzow, *Kunstst.*, 12, 49 (1922); Breuer, *Kunstst.*, 16, 23 (1926).



used in the electrical industry<sup>1</sup> for switchboards, transformers, bobbins, and winding carriers, and in the form of coiled tubes as inductor and transformer tubes, as insulators (but for interior use only), as guide rails, and recently for radio apparatus. Many other objects are made of laminated sheet, such as aeroplane propellers, noiseless gear wheels,<sup>2</sup> and spur wheels,<sup>3</sup>



FIG. 13

the harder qualities of artificial leather, feet for furniture, disc washers, brake linings,<sup>4</sup> and ornamental tiles.<sup>5</sup>

<sup>1</sup> On insulating bodies for electric machinery, see also Süddeutsche Isolationswerke G.m.b.H., German Pat. 350,680 (1919).

<sup>2</sup> Baekeland, U.S. Pat. 1,160,364 (1915); Conrad, U.S. Pat. 1,167,742-3 (1916); Bastian, U.S. Pat. 1,223,348 (1917); Stevenson, U.S. Pat. 1,298,816 (1919); British Westinghouse Electric & Manuf. Co., British Pat. 108,597; *Kunstst.*, 9, 69 (1919); Grünwald, German Pat. 302,111 (1916); British Pat. 111,664 (1917); *Kunstst.*, 12, 109 (1922); *C.* (1922), II, 1089.

<sup>3</sup> Fibroic Insulation Co., L. F. Frederick, U.S. Pat. 1,564,774 (1924); *C.* (1926), I, 2226.

<sup>4</sup> "Scandinavia" Belting, Ltd., M. Fenton, Crowther, German Pat. 402,883; British Pat. 178,883; *Kunstst.*, 15, 44, 65 (1925); H. Frood, The Herbert Frood Co., Ltd., German Pat. 247,891 (1910).

<sup>5</sup> Dr. Heinr. Traun & Söhne, German Pat. 423,932 (1924).

Resoles are also used as impregnating agents in a narrower sense than for the manufacture of laminated masses, and may, for example, be used for the impregnation of bobbins and armatures for dynamos, motors, arc lamps, and transformers, in the form of either liquid resins or resin solutions. These are then hardened by careful heating in the bakelizer. For the production of insulating materials of this and similar character,<sup>1</sup> it is advisable to add softening agents such as naphthalene, anthracene, and so forth, which also reduce the velocity of hardening and facilitate the removal of any solvents. The impregnation<sup>2</sup> of wood,<sup>3</sup> leather, textiles,<sup>4</sup> cardboard, paper, and asbestos, has also been proposed, in order to obtain, by hardening, especially resistant and useful materials, which are easily worked mechanically.

A peculiar form of coating has been suggested for producing resistant linings to chemical and other plant.<sup>5</sup> A layer of asbestos cloth is first attached to the wall of the container by means of hardening resin; this is then heated until the resite

<sup>1</sup> Aylsworth, U.S. Pat. 1,047,484 (1912); Baekeland, U.S. Pat. 1,156,452; *Kunstst.*, 6, 12 (1916); U.S. Pat. 1,213,144 (1917); 1,213,726; 1,216,265-6; Jackson, U.S. Pat. 1,323,284; Apple, U.S. Pat. 1,132,297; Frederick McCullough, U.S. Pat. 1,231,588; Scheibe, U.S. Pat. 1,241,559; Halbleib, Lee, U.S. Pat. 1,274,411; Zenk, U.S. Pat. 1,046,928, 1,255,681; Aichele, U.S. Pat. 1,296,731; Hayden, U.S. Pat. 1,096,839; The British Thomson-Houston Co., Ltd., British Pat. 5,165-7 (1911); 13,946 (1910); Kabelfabrik und Drahtindustrie A.-G., Austrian Pat. 98,168 (1923); *C.* (1925), I, 999; J. J. Kessler, U.S. Pat. 1,591,534.

<sup>2</sup> For many impregnation processes the use of mixtures of the components, phenols and formaldehyde, is recommended, which may be homogenized by caustic alkali solutions, and so forth, or in the form of solutions of formaldehyde in phenols, without any appreciable condensation taking place before application. Such condensation first takes place on heating after impregnation and is effected by the same operation as the hardening process.

<sup>3</sup> Baekeland, German Pat. 231,148 (1908); U.S. Pat. 942,852; 946,671; Aylsworth, U.S. Pat. 1,111,286 (1914); Dyer, U.S. Pat. 994,067 (1911); E. Haefely & Cie. A.-G., French Pat. 600,629 (1925); Swiss Pat. 109,561 (1924); *C.* (1926), I, 2947; see also H. Kühl, *Kunstst.*, 5, 196 (1915); J. J. Kessler, U.S. Pat. 1,593,579; see also the earlier patent of A. Bevier, German Pat. 136,621 (1900), on wood conservation.

<sup>4</sup> G. W. Neu, French Pat. 580,565 (1924); *C.* (1925), I, 1669; O. Ruff, German Pat. 327,399 (1917); *C.* (1921), II, 142.

<sup>5</sup> H. Lebach, *Angew.*, 38, 1092 (1925); Wirth, British Pat. 171,369 (1921); German Pat. 346,570 (1920); *C.* (1922), II, 1216; *Kunstst.*, 12, 37 (1922); German Pat. 348,618 (1920); 350,819 (1921); 359,226 (1921); *C.* (1922), IV, 634; (1923), II, 1255; *Kunstst.*, 12, 141 (1922); see also German Pat. 420,413 (1924); *C.* (1926), I, 1300; *Chem. Ztg.*, 51, 349 (1927); I. G. Farbenindustrie A.-G., British Pat. 276,697; *C.* (1928), I, 100.

is formed, after which the porous lining is impregnated with hardening phenol-formaldehyde resin, which after hardening forms an acid-proof and durable lining.<sup>1</sup> According to another similar process of applying a lining a wide-meshed fabric is used, which is coated with artificial resin and then applied. ("Haveg" material, see page 346.)

**Production of Coatings from Hardening Resins.** The exceptionally valuable properties of the hardening phenol-formaldehyde resins, and more especially the practical indestructibility of the hardened products, very soon suggested the possibility of applying them as varnish bases. However, as will be gathered from the above description of their application as linings, there are considerable difficulties in applying them as varnishes, and so far they have not been used for the purpose to any appreciable extent. The difficulties are more particularly associated with the brittle character of the hardened products, which easily leads to the formation of cracks, which would, of course, destroy any effective protection afforded to the underlying material. The addition of plasticizing agents for the purpose of rendering the film more elastic, as has often been recommended, is not of much use,<sup>2</sup> as this is largely volatilized by the subsequent hardening process. The adhesion of the varnish film may probably be improved by various preliminary treatments, such as treatment of a metallic surface with acids, or roughening it by the application of magnesium chloride solution, the application of a rough intermediate layer of ductile metal, thermal treatment by hot air, and so forth;<sup>3</sup> the adhesion is undoubtedly improved by the addition of a certain proportion of inert fillers, such as powdered quartz, powdered glass, slate powder, iron oxide, sand, emery, asbestos, or powdered resite,<sup>4</sup> as these diminish the shrinkage consequent on hardening and thus counteract the tendency to crack. Yet a coating

<sup>1</sup> On the durability of resite linings, for example, of one in a centrifuge used for phosphoric acid residues containing large quantities of phosphoric and sulphuric acids, throughout a period of eleven years, see *Chem. Met. Eng.*, 33, 624; *C.* (1928), II, 3105.

<sup>2</sup> See O. Faust, French Pat. 598,550 (1925); *C.* (1926), I, 2254; *Kunstst.*, 16, 137 (1926).

<sup>3</sup> La Bakélite, French Pat. 628,819; *C.* (1928), I, 1237.

<sup>4</sup> Baekeland, U.S. Pat. 957,137 (1910); 982,230 (1911).

of hardening phenol-formaldehyde resin appears to be suitable in such cases only in which the coated object is to be subjected to very slight mechanical wear. In such cases the hardness of the resite layer and its high power of resistance to acids, salt solutions, alkalis, and so forth, and its resistance to heat are fully exhibited. The numerous proposed methods of application as a varnish,<sup>1</sup> some of which take the peculiarities of these products into account, must be considered from the above standpoint.

The materials used for the production of varnishes, etc., are the condensation products which are either still liquids, or solids possessing the required solubility.

The principal solvent is spirit,<sup>2</sup> but other solvents are also used, such as acetone, the higher alcohols, and esters.<sup>3</sup>

<sup>1</sup> Baekeland, U.S. Pat. 954,666 (1910); 982,230 (1911); 1,019,408 (1912); 1,085,100; 1,160,363 (1915); Aylsworth, U.S. Pat. 1,139,470; *Kunstst.*, 12, 23 (1922); R. Mewes, German Pat. 259,825 (1911), container for liquid air, etc.; Eitner, Kind, German Pat. 276,434 (1913), leather varnish; Buffum, U.S. Pat. 1,197,601 (1916); Ges. für chem. Ind., Swiss Pat. 75,601; *Kunstst.*, 8, 307 (1918); German Pat. 315,017 (1916); *C.* (1919), IV, 1131; McIntosh, U.S. Pat. 1,269,292 (1918); McClain, U.S. Pat. 1,299,747 (1919); Arnstädter Malzfabrik, German Pat. 304,319 (1916); *C.* (1919), IV, 770; German Pat. 305,179 (1917); 307,699 (1918); Ehrenfeld, German Pat. 339,905 (1919); *C.* (1921), IV, 976; Märk. Marmorwerke, German Pat. 388,225 (1921); *C.* (1924), I, 1582; J. Marcusson, Swiss Pat. 91,801; *C.* (1922), II, 948; J. Langbein, British Pat. 223,461 (1924); *C.* (1925), I, 888; German Pat. 415,306 (1924).

For coating metals in particular: Baekeland, U.S. Pat. 957,137 (1910), Food containers, etching with acids, fillers; Jones, U.S. Pat. 1,171,725 (1916); *Kunstst.*, 6, 233 (1916); Kempton, U.S. Pat. 1,249,770 (1917); McIntosh, U.S. Pat. 1,269,292 (1918); Townsend, U.S. Pat. 1,146,214 (1915); 1,273,954 (1918); Ruff, German Pat. 304,985 (1917); Swiss Pat. 90,485; *C.* (1918), I, 898; *Kunstst.*, 8, 273 (1918); 9, 273 (1919); 12, 37 (1922); Gesellschaft für Technik, German Pat. 382,749 (1920), etching with  $MgCl_2$  solution; La Bakelite, Austrian Pat. 103,905 (1925); *C.* (1926), II, 2120, rough intermediate layer of ductile metal; British Thomson-Houston Co., Ltd., W. E. Ruder, British Pat. 249,144 (1926); *C.* (1926), II, 809, insulation of electro-magnets; R. Arnot, British Pat. 288,303; *C.* (1928), II, 292, coating shaped objects.

<sup>2</sup> On the use of special solvents or mixtures, see Bakelite Ges. m.b.H., German Pat. 286,568 (1912); *C.* (1915), II, 570; Austrian Pat. 68,129; *Kunstst.*, 5, 129 (1915); British Pat. 6,293 (1912); Baekeland, U.S. Pat. 1,018,385 (1912); *Kunstst.*, 10, 120 (1920); U.S. Pat. 1,037,719; 1,085,100; Jones, U.S. Pat. 1,200,731 (1916); *Kunstst.*, 7, 67 (1917); 8, 307 (1918); U.S. Pat. 1,209,165. *Kunstst.*, 7, 141 (1917); Howse, British Pat. 156,896 (1919); *C.* (1921), II, 808; W. Schrauth, German Pat. 349,905 (1919), Cyclohexanols or Esters; Bakelite Corp., H. C. Cheetham, U.S. Pat. 1,528,006 (1923); *C.* 1925, I, 2473; *Kunstst.*, 15, 181 (1925); Bakelite Cor., L. V. Redman, U.S. Pat. 1,591,999 (1922); *C.* (1926), II, 1794. On varnish production by peptonization, see Warchavsky, French Pat. 495,021; *Kunstst.*, 12, 38 (1922).

<sup>3</sup> On determinations of the strength of such solutions, see A. L. Abonyi, *Kunstst.*, 16, 30 (1926).

After applying the varnish coats, which may be effected by painting, dipping, spraying, or pouring,<sup>1</sup> and drying in the air, the hardening process follows, which develops the exceptional qualities of the material. Hardening is usually effected by careful heating over a long period, the temperature being necessarily adjusted to the properties of the varnished material, which may, for example, be wood. For some purposes it is sufficient to heat to temperatures in the neighbourhood of 100° C. for one or two days. Naturally, the higher the temperature the shorter is the heating period required. In some circumstances it is advisable to heat under pressure, in a bakeshelf, to avoid blistering. After heating it is necessary to arrange that the cooling process may be slow.

Such varnishes are used for coating lamp shades, lamp stands, and other parts of illuminating contrivances, where resistance to heat, oil, petroleum, spirit, and so forth, is required. They are also used for varnishing door plates, door knobs, brass bedsteads, and so forth. Coatings are also applied to metals for special protection against liquids, to rubber as a protection against ultra-violet light, for protecting wooden chimneys against acid vapours, and so forth.<sup>2</sup>

**Further Applications of Resoles.** These resins are also used as cements, for example, for fixing bristles into brushes (galvanizing and roller brushes) and hair into paint brushes, for electric lamp caps, for knife handles, and so forth.<sup>3 4</sup> They are also used for such purposes with fillers, which may comprise natural resins such as colophony or Manilla copal. They are

<sup>1</sup> Application in powder form and subsequent melting has also been proposed.

<sup>2</sup> *Chem. Met. Eng.*, 33, 647 (1926).

<sup>3</sup> Bäckeland, U.S. Pat. 1,019,407 (1912); 1,019,408 (1912); Aylsworth, U.S. Pat. 1,065,495 (1913); Brown, U.S. Pat. 1,250,959 (1917); Egerton, U.S. Pat. 1,353,800 (1920); Hayhurst, British Pat. 122,661 (1917); J. Marcusson, German Pat. 402,730 (1919); *Kunstst.*, 15, 102 (1925); *C.* (1924), II, 2568; Westinghouse Electric & Manuf. Co., E. Frost, U.S. Pat. 1,576,737 (1921); *C.* (1926), II, 317; *Kunstst.*, 16, 204 (1926); *Chem. Age*, 7, 207 (1922).

<sup>4</sup> Chem. Fabriken Dr. Kurt Albert, German Pat. 304,752 (1917); *Kunstst.*, 8, 143 (1918); Hayhurst, British Pat. 158,427 (1919), for pottery; Bureau d'Organization Economique, German Pat. 405,135 (1921); *C.* (1925), I, 744, Elektrode settings; Dr. H. Traun & Söhne, German Pat. 432,485 (1923); *C.* (1926), II, 2234; H. O. Keay, British Pat. 230,678 (1924); *C.* (1925), II, 975, for uniting stones; R. Arnot, German Pat. 418,732 (1924); *C.* (1926), I, 1915; *Kunstst.*, 16, 96 (1926); Canadian Pat. 256,883.

also used as adhesives.<sup>1</sup> A number of further applications have been suggested, which will only be briefly mentioned as they have attained but little if any practical importance.<sup>2,3</sup> These include the use of hardening phenol-formaldehyde resins for the production of packing materials,<sup>4</sup> waxed paper,<sup>5</sup> for sizing paper,<sup>6</sup> for the production of water-tight sanded or cement flooring, fireproof coatings,<sup>7</sup> roofing materials,<sup>8</sup> for brake linings,<sup>9</sup> for producing colour screens,<sup>10</sup> for the production of non-setting modelling materials,<sup>11</sup> for resistant reserves,<sup>12</sup> for wall coatings,<sup>13</sup> for fixing metallic powders, and so forth, in textile

<sup>1</sup> See Chem. Fabr. Dr. K. Albert, German Pat. 304,752 (1917), porous coatings on metals.

<sup>2</sup> On more recent applications, see also Redman, *J. Ind. Chem.*, 15, 677; *C.* (1923), IV, 667.

<sup>3</sup> M. Perkiewicz, German Pat. 237,728, 246,903 (1911), as an addition to glue solution for coating pottery to prevent efflorescence; Ball, German Pat. 254,750 (1912), violin bows; Curley, U.S. Pat. 1,094,705 (1914), special frames for tennis rackets; Aylsworth, Smith, U.S. Pat. 1,134,433 (1915), golf balls; Beatty, U.S. Pat. 1,158,963; *Kunstst.*, 6, 62 (1916), photographic films; Baekeland, U.S. Pat. 1,160,363; *Kunstst.*, 6, 63 (1916), waterproof compositions; Albrecht, German Pat. 264,956 (1912); U.S. Pat. 1,205,957, dental fillings; Eilertsen, French Pat. 526,653; British Pat. 165,758 (1921); *C.* (1921), IV, 1014; French Pat. 528,659; *C.* (1922), II, 666; French Pat. 24,925, 25099; *C.* (1923), IV, 540; Bronner, U.S. Pat. 1,374,718 (1921), for viscose silk; Sweetland, Manning, Hilpert, U.S. Pat. 1,292,535, filters; Schülke, Elsner, British Pat. 161,526 (1922); *Kunstst.*, 12, 142 (1922), spinning nozzles; Sudenburger Masch.-Fabrik und Eisengiesserei, German Pat. 344,327 (1921); 361,735 (1922); Frood, British Pat. 176,404 (1920), for footwear production, etc.; L. Casella & Co., German Pat. 347,197; *C.* (1922), II, 486, fancy threads; German Pat. 380,994 (1920); U.S. Pat. 1,451,299; British Pat. 198,166.

<sup>4</sup> Baekeland, U.S. Pat. 941,605 (1909); Swiss Pat. 51,816; Chapell, U.S. Pat. 1,102,473.

<sup>5</sup> Gesell, U.S. Pat. 1,277,904 (1918).

<sup>6</sup> Baekeland, U.S. Pat. 1,160,365 (1915); Holzverkohlungs-Ind. A.-G., German Pat. 303,925, 338,395-6, 339,594, 342,255; *C.* (1921), IV, 604, 824; Ruff, German Pat. 327,399 (1917); *C.* (1921), II, 142; German Pat. 303,926; German Pat. 307,694; *C.* (1919), IV, 931; W. Schmidt, E. Hauser, German Pat. 305,524 (1917); on application for strengthening paper yarn, see O. Ruff, German Pat. 302,551 (1917).

<sup>7</sup> Achtmeyer, U.S. Pat. 1,429,265 (1922); *C.* (1923), IV, 668; *Kunstst.*, 13, 125 (1923).

<sup>8</sup> Aylsworth, U.S. Pat. 1,077,113.

<sup>9</sup> Achtmeyer, U.S. Pat. 1,429,266-7 (1922); *C.* (1923), IV, 669; *Kunstst.*, 13, 125 (1923); U.S. Pat. 1,418,607; *C.* (1923), IV, 950; Frood, English Pat. 166,916; *C.* (1922), II, 1230.

<sup>10</sup> Wieland, German Pat. 343,759 (1918); French Pat. 519,537 (1919); *C.* (1921), IV, 732.

<sup>11</sup> M. Thiele, German Pat. 289,565 (1911).

<sup>12</sup> Cassella & Co., German Pat. 247,277; *C.* (1922), II, 578; German Pat. 380,994 (1920); *Fall.* XIV, 557; U.S. Pat. 1,451,299; British Pat. 198,166.

<sup>13</sup> V. Lefebure, British Pat. 237,320 (1924); *C.* (1926), I, 1017.

printing,<sup>1</sup> for preserving biological specimens,<sup>2</sup> as holders for perfumes,<sup>3</sup> for decorating textiles,<sup>4</sup> for the production of a glass substitute,<sup>5</sup> for the photographic production of printing faces,<sup>6</sup> and so forth.

The various proposals for the application of phenol-formaldehyde resins already referred to, give some idea of the many-sided applications of these materials, but as many of the numerous patented processes have scarcely found practical application we reproduce a list of all the uses to which these materials are ordinarily put in Europe and America, which was kindly placed at our disposal by the Bakelite G.m.b.H.

#### APPLICATIONS OF PHENOL-FORMALDEHYDE RESINS

Acid-proof linings	Brake linings
Aeroplane propellers	Brake parts
Ammeter cases	Brush backs
Anti-dust spectacles	Brush handles
Anti-friction bearings	Buttons
Apparatus—acid proof	
Apparatus cases	Cable branching boxes
Apparatus handles	Cable terminal caps
Armature coil casings	Calculating machine parts
Armature detectors	Calendar frames
Armature distribution blocks	Camera bodies
Armature insulators	Candlesticks
Armature intensifiers	Carbon brushes
Armature variometer casings	Cases for measuring instruments
Artificial stone impregnation	Cases for radio parts
Ash trays	Cases for transformers
	Castanets
Balance dials	Castors
Balls for bearings and clutches	Chandeliers
Bangles	Chemical apparatus
Banjo frames	Chin supports
Beads	Cigar and cigarette holders
Billiard balls	Clock cases
Bobbins	Closet seats
Bobbin carriers	Coffee-pot handles
Bowls	Commutators
Boxes	Condensers
Bracelets	Condenser batteries, as protection against over-voltage
Brake couplings	

<sup>1</sup> E. Zündel, German Pat. 264,137 (1912).

<sup>2</sup> J. Brunner, E. Scheele, U.S. Pat. 1,588,164 (1925); French Pat. 605,403 (1925); *C.* (1926), II, 1794.

<sup>3</sup> Merz & Co., German Pat. 428,951 (1924); *C.* (1926), II, 1209.

<sup>4</sup> G. E. Farragut, British Pat. 247,282 (1914); *C.* (1926), II, 2953.

<sup>5</sup> P. Carpentier, French Pat. 586,303 (1923); *C.* (1926), II, 1479; *Kunstst.*, 16, 255 (1926).

<sup>6</sup> E. Doelker, German Pat. 390,898; 408,097 (1921).

- Condenser cases
- Condenser knobs
- Contact carriers
- Containers—acid proof
- Copying rollers
- Counters
- Crucible handles
- Cut-outs
- Cut-out tubes and plates
- Dental instruments
- Developing dishes
- Diaphragms
- Dice
- Distributing discs
- Door handles
- Door knobs
- Drying pans
- Dynamo brush-holders
- Ear-rings
- Electric drill parts
- Electric piano parts
- Electromedical apparatus
- Enamels
- Equipment for doctors and dentists
- Etuais
- Fan supports
- Filter press plates
- Fire extinguishers
- Fishing reels
- Fishing tackle
- Flat iron handles
- Flat iron plugs
- Fountain pen holders
- Frictionless bearings
- Gas meter packings
- Gear wheels for motors, motor bi-  
cycles and machinery
- Gears
- Glove fasteners
- Gramophone discs
- Grinding discs
- Gun facings
- Gun stocks
- Hand lamp handles
- Hand mirror backs
- Hardened paper
- Heater covers
- High voltage insulators
- Holders for heating apparatus
- Ice-box covers
- Ignition coil casing
- Indicator dials
- Insulating ducts
- Insulating plates
- Insulator boxes
- Insulators
- Knife handles
- Laboratory apparatus for hydro-  
fluoric acid
- Lamp handles
- Lamp holders
- Lamp shade varnishes
- Lamp sockets
- Lamps for dentists
- Letter balances
- Lids
- Lighters
- Loud speakers
- Machine parts
- Magnetos
- Mandoline bridges
- Mandoline keys
- Megaphones
- Motor brakes and steering gear
- Motor gear wheels
- Motor goggle frames
- Motor pistons
- Mouthpieces for wind instruments
- Musical instrument parts
- Music rolls
- Necklaces
- Ornaments
- Packing plates
- Packing rings
- Paint brush cement
- Pans
- Parts for cinematographs
- Parts for office machinery
- Pencil holders
- Penholders
- Petrol tank caps
- Piano keys
- Piano parts
- Picture frames
- Pipe lines
- Pipe mouthpieces
- Pipes
- Pistol handles
- Pistons for motors and motor bicycles
- Plugs
- Press mouldings
- Printing blocks
- Propellers
- Pumps



Radio parts	Tachometer parts
Rail insulators	Teapot handles
Razor handles	Telegraph parts
Reaction towers	Telephone handles
Rectifiers	Telephone mouthpieces
Regulating wheels for motors	Telephone parts
Rheostat frames	Telephone receivers
Rods	Terminal blocks
	Thimble tops
Safety spectacle frames	Tile impregnation
Shaving brush handles	Tool handles
Signal parts	Tram strap handles
Skittle balls	Transformer parts
Socket boxes	Transport containers
Socket cement	Typewriter parts
Sockets	
Sound intensifiers	Umbrella handles
Spark inductors	
Spark intensifiers	Vacuum brake parts
Spinning pots	Vacuum cleaner parts
Spraying pots	Valve seatings
Starting gear	Varnishes
Stirring gear	Violin parts
Stoppers	Violin scrolls
Supporting discs and rings	Voltage regulators
Supports for glasses and bottles	
Surgical instruments	Walking-stick handles
Switch caps	Wall coatings
Switch covers	Washing machine stirrers
Switch sockets	Window lugs
Switchboards	Writing utensils
Switches	
Sword handles	X-ray tubes

## COPAL SUBSTITUTES

**Phenol-formaldehyde Resins Soluble in Fatty Oils and Hydrocarbons.** Phenol-formaldehyde resins of the type of the Novolaks and the hardening products (resoles) are soluble in spirit and similar solvents, but are ordinarily insoluble in hydrocarbons and fatty oils, and cannot, therefore, be used for oil varnishes, which would otherwise form a very extensive field of application. Novolaks can indeed be incorporated with linseed oil, for example, by heating to a high temperature with that substance, but the solutions which are so obtained are of very dark colour; this reaction may account for the alleged solubility of phenol-formaldehyde resin in oil, which is referred to in some earlier publications.<sup>1</sup>

<sup>1</sup> See Aylsworth, U.S. Pat. 1,111,287; Robinson-Bindley, Weller, Dulcken, British Pat. 134,563 (1918); *Kunstst.*, 10, 165 (1920); on the solubility in

Free solubility in benzene and in oil, such as is required for utilization as oil varnish, can be imparted to phenol-formaldehyde resins by combining them with natural resins, such as colophony, their esters, and salts, with artificial resins, such as cumarone resins, or with fatty oils or oil acids.<sup>1</sup> Such additions act partly as dissolving agents, but may also to some extent enter into chemical combination with the phenol-formaldehyde resin, in the form of some unknown type of condensation, probably of esterification.<sup>2</sup> Artificial resins obtained by such a process are sold as "Albertols."<sup>3,4</sup> Similar products are also obtained by the incorporation of phenol-alcohols or dihydroxydiphenylmethanes with colophony.<sup>5</sup>

Resins soluble in benzene and oils are also obtained by condensing further with formaldehyde in the usual manner the condensation products of phenols with unsaturated hydrocarbons, such as styrol, pinene, diamylene, etc.<sup>6</sup> The hydrocarbons may be replaced by suitable fatty oils.<sup>7</sup> The same property of solubility is obtained if the initial condensation products obtained in the usual manner from phenols and formaldehyde in the presence of basic condensing agents are

benzene of naphthol-formaldehyde resins which have been heated to more than 200° C., see P. Esholz, J. Altendorf, German Pat. Application E, 23,046, Cl. 22h (15th March, 1918); see Bakelite G.m.b.H., German Pat. 468,391, resins soluble in oil from formaldehyde and  $\beta$ -naphthol.

<sup>1</sup> Chem. Fabriken Kurt Albert and Ludwig Berend, German Pat. 254,411, 269,659; also German Pat. 281,939 (1913); *C.* (1915), I, 410; *Kunstst.*, 5, 68 (1915); German Pat. 289,968 (1914); *C.* (1916), I, 318; *Frdl.* XII, 577, 579; German Pat. 438,371, 440,003, etc.; British Pat. 1269 (1912); 15,875 (1914); 107,205 (1916); *Kunstst.*, 12, 14 (1922); U.S. Pat. 1,191,390 (1916); 1,205,081-2 (1916); 1,259,347 (1918); Austrian Pat. 77,698; Swiss Pat. 72,631, etc. See *Kunstst.*, 7, 23, 323 (1917); 10, 101 (1920); 11, 79 (1921).

<sup>2</sup> See, for example, German Pat. 440,003.

<sup>3</sup> In the United States analogous products are known as "Amberol."

<sup>4</sup> See also E. Fonrobert, *Farbenzeitung*, 32, 1671, 1734 (1927); also W. Beissel, *idem.* 1974; W. Wolff, *idem.* 2085; E. Stock, *idem.* 2141; Albertol Pamphlet No. 18; also H. Wolff, W. Toeldte, G. Zeidler, *Farbenzeitung*, 33, 1724 (1927-8). On Amberol varnishes especially, see A. E. Staudermann, H. L. Beakes, *Ind. Engin. Chem.*, 20, 674; *C.* (1928), II, 1154.

<sup>5</sup> Chem. Fabriken Dr. Kurt Albert, G.m.b.H., A. Amann, E. Fonrobert, U.S. Pat. 1,623,901; British Pat. 259,030; French Pat. 592,584, 596,339; *C.* (1928), II, 1039, 1040.

<sup>6</sup> Bakelite G.m.b.H., German Pat. 340,989 (1919); *C.* (1921), IV, 1178; *Frdl.* XIII, 647; *Kunstst.*, 12, 28 (1922); regarding the condensation products of phenols and unsaturated hydrocarbons, see pp. 171 *et seq.*

<sup>7</sup> Bakelite Cor., British Pat. 293,453; Bakelite G.m.b.H., German Pat. 468,391.

treated with organic acids soluble in benzene, such as stearic acid, oleic acid, resinic acid or colophony, and so forth,<sup>1</sup> or if they are subsequently treated with polyvalent or polycyclic phenols, for example, naphthols, in the presence or absence of colophony.<sup>2</sup> Solubility in benzene is stated also to be obtained if pyromucic acid is present in the ordinary process of resin production.<sup>3</sup> Apart from other similar processes,<sup>4</sup> we must refer to alterations in the solubility which occur if phenol derivatives are used, or if phenol-formaldehyde resins are subsequently transformed into similar derivatives, or by the use of aldehydes other than formaldehyde. With regard to such products, which are mostly of no importance, we must refer to the succeeding sections.

In the varnish industry,<sup>5</sup> the "Albertol Copals" already play an important part as copal substitutes which are soluble in oil.<sup>6</sup> Two types of oil-soluble Albertols are mainly used, each of which is obtainable in various qualities. All these products<sup>7</sup> are more or less hard, clear resins, in lump form, which are odourless, non-adhesive, and free from ash, and which give acid values below twenty, indicating compatibility with colouring matters. They are all soluble in white spirit, benzene, solvent naphtha, tetraline, carbon tetrachloride, chloroform, turpentine oil, fatty oils and esters, such as ethyl, butyl and amyl acetate, and are all insoluble in acetone, spirit, and other alcohols. The two types differ somewhat with regard

<sup>1</sup> Bakelite G.m.b.H., R. Hossen, German Pat. 340,990, 410,858 (1922); *Kunstst.*, 15, 182 (1925); British Pat. 206,469 (1923); French Pat. 27,803, 531,467 (1923); Swiss Pat. 105,859 (1923); *C.* (1925), I, 2471; see also H. Bucherer, Footnote (1), p. 333.

<sup>2</sup> Bakelite G.m.b.H., British Pat. 282,414; 283,124.

<sup>3</sup> Plausons Forschungsinstitut, G.m.b.H., German Pat. 342,365 (1920).

<sup>4</sup> See Brown, U.S. Pat. 1,212,738 (1917); *Kunstst.*, 7, 237 (1917), who, for example, produces an oil varnish from tung oil, a lead-manganese drier, cresol, and formaldehyde.

<sup>5</sup> On the use of these products in linoleum manufacture, see F. Fritz, *Seifensieder-Ztg.*, 51, 481; *C.* (1924), II, 2216.

<sup>6</sup> The authors take the opportunity of thanking the producing firm, Chem. Fabriken Dr. Kurt Albert, G.m.b.H., Wiesbaden-Biebrich, for information supplied.

<sup>7</sup> See Andés, *Kunstst.*, 9, 101, 119, 133 (1919); *Farbenztg.*, 24, 1193, 25, 993 (1919-20); Fonrobert, *Farbenztg.*, 25, 719 (1920); *Kunstst.*, 12, 121 (1922); 13, 109 (1923); *Farbe und Lack* (1924), 274; *Farbenztg.*, 32, 1671, 1734 (1927); Berend, *Angew.*, 36, 242 (1923); A. Eibner, H. Munzert, *Farbenztg.*, 29, 1847 (1924); see also Footnote (4), p. 365.

to their power of dissolving in fatty oils, but more especially with regard to fastness to light. The individual qualities are graded according to melting point (hardness) and colour.<sup>1</sup>

Thus, the oil-soluble Albertol-copals 116Q, 117R, and 118S, are supplied in qualities of normal colour (colour index, 48-56),<sup>2</sup> dark (colour index, 112-224), and very dark colour (colour index, 500-2,000). The three qualities have the following melting points—<sup>3</sup>

Oil-soluble Albertol Copal	116Q . .	95-105-140° C.
"	" " 117R . .	110-120-155° C.
"	" " 118S . .	120-130-170° C.

They become somewhat discoloured with time, and differ in this respect from the dearer qualities referred to below, but they may be considered as suitable substitutes for Congo and Kauri copals. In order to convert 116Q into an oil varnish, it suffices to dissolve it in the oil at 150-200° C. In the case of the other qualities it is necessary to "boil" them with the oil by prolonged heating to 200-250° C. in the case of 117R, and to 250-270° C. in the case of 118S, in order to avoid the separation of insoluble material on subsequent dilution. The "boiling" is completed when a sample dissolves perfectly in the solvent intended to be used for the oil varnish.

Albertol copal 111L may be considered to be typical of the second type of oil-soluble copal substitutes; it is obtainable in very pale qualities (colour index under 28), and is characterized by exceptionally good solubility, so that no preliminary boiling is necessary for the preparation of oil varnishes; it is usually sufficient simply to mix the solution of the resin with the fatty

<sup>1</sup> Those qualities only which are mentioned in the latest catalogues will be referred to below.

<sup>2</sup> The colour index (denoted in German by F.-Z.) is determined by the method of Fonrobert and Pallauf, *Farbenztg.*, 31, 967, 1354 (1926). It indicates the number of megohms of free iodine in 100 cc. of a solution of that element in aqueous iodine-potassium iodide solution of the same depth of colour, the sample being examined in a layer 10 mm. thick.

<sup>3</sup> The first figure denotes the temperature at which sintering commences, the second figure the temperature at which the substance melts and becomes clear, when the determination is effected in the usual manner in a melting-point tube in a sulphuric acid bath. The third figure indicates the temperature at which the resin is melted to such a degree that it can be well mixed by stirring.

oil or oil preparation. The product is exceptionally fast to light, although on heating to more than 60° C., when hardening, slight discoloration occurs. The melting point of Albertol Copal 111L is 95/105/140° C. A still better quality has recently been marketed, which is considerably harder, known as Albertol Copal 209L, of melting point 125/135/175° C. Owing to its hardness the product is particularly suitable for coach varnishes and flattening varnishes, but is difficult to dissolve in the cold. For incorporation with fatty oils, heating to 240–250° C. is therefore recommended, until a sample can be diluted without precipitation. In this, as in other cases, it is advantageous to carry out the heating process in an atmosphere of carbon dioxide, in order to avoid darkening of the product.

Albertol copals are fairly stable, being unattacked by water, sodium carbonate solution or ammonia, even on prolonged contact, and their surface gloss is in no way affected by these substances.

The properties which have been described cause the oil-soluble Albertol copals to be excellent substitutes for natural copals and amber for the production of oil varnishes. They offer the advantage that no preliminary "gum running" process, with the accompanying considerable loss, is required, these products being equivalent to natural copals which have already undergone that process. They also offer the advantages over natural copals that, being synthetic products, they are obtainable of uniform quality and great purity, and that, in contrast to Congo and Manilla copals, they can be directly mixed with any pigments. Their use is limited to some extent only for the production of white and light-coloured enamels.<sup>1</sup> It should be mentioned that oil varnishes prepared with certain Albertols occasionally show separation of abietic acid derivatives; this can be avoided by the addition of small quantities of cadmium resinate soluble in linseed oil.<sup>2</sup>

In addition to the types of Albertol copals already described, other Albertols have been recommended for the production of

<sup>1</sup> For working recipes, see, for example, *Kunstst.*, 13, 117 (1923); see also Albertol Pamphlet No. 16, on "Varnish Recipes."

<sup>2</sup> Dr. K. Albert, G.m.b.H., German Pat. 448,297 (1925).

oil varnishes, which are not only soluble in oil, but also in alcohol, and which are further characterized by high acid values up to 130 or 150.<sup>1</sup> These correspond approximately to the Manilla copals. Owing to their acid character they are obviously unsuitable for certain purposes, which is a circumstance to be borne in mind when using these cheap products. They are especially suitable for the production of acid-proof varnishes with tung oil, for which purpose they possess the advantage over neutral Albertol copals of exercising a similar retarding influence to colophony on the tendency of tung oil to form

Those Albertol copals which are used for oil varnishes are partially suitable for use in cellulose ester varnishes.<sup>2</sup> The products specially recommended for the latter purpose, qualities 78C and 82G, closely resemble the above-described oil-soluble products in properties. Thus they show the same solubility in various solvents, are also insoluble in spirit, but are soluble in acetone. Their melting point is 85/95/125° C. Their fastness to light is good. Whilst the quality 78C has a rather high acid value (up to 80), and is therefore not freely miscible with pigments, quality 82G has an acid value of not more than 20. These resins are prepared in the usual manner.

**Various Derivatives of Phenol-formaldehyde Resins.** Derivatives of phenol-formaldehyde resins may be obtained either by using phenol ethers or phenol esters in place of free phenols as raw materials, or by subsequently converting the finished phenol-formaldehyde resins into ethers or esters by suitable reagents. Differences are to be anticipated as the phenol ethers can only be caused to interact with formaldehyde with difficulty.<sup>3</sup> On the other hand, if the finished resins are subsequently converted into ethers or esters it is uncertain to what extent the action is merely confined to free phenolic groups,

<sup>1</sup> Qualities 61L, 62M, 63N, and 112M.

<sup>2</sup> For example, Albertol 111L, 209L, 112M; under some conditions only, the spirit-soluble types may also be used for this purpose, such as 35K, K6S extra pale and hard, and Albertol Shellac. In so far as the products prepared with colophony (abietic acid) cause separation in the corresponding spirit varnish, the fault can be avoided by the addition of lithium resinate, which is soluble in alcohol; see German Pat. 448,297 of Dr. K. Albert (G.m.b.H.).

<sup>3</sup> See p. 179.

and to what degree it extends to alcoholic hydroxyl groups, formed by the action of the formaldehyde.

When condensed under acid conditions, phenol ethers and formaldehyde<sup>1</sup> form highly viscous oils or very hard, pale resins, according to the proportion of formaldehyde used; the products are soluble in aromatic hydrocarbons, turpentine oil, fatty oils and other organic solvents, with the exception of the alcohols. Similar resins are also formed if use is made of phenol ethers which are substituted by an alkyl or alkyloxy-group in the m-position,<sup>2</sup> or of the alkyl ethers of tetrahydronaphthols.<sup>3</sup> The production of plasticizing agents from ethyleneglycolmonoaryl ethers ( $C_6H_5 \cdot O \cdot CH_2 \cdot OH$ ) and formaldehyde<sup>4</sup> is of interest, as is also the fact that the condensation products from esters of aromatic hydroxycarboxylic acids, such as salicylic acid, and formaldehyde<sup>5</sup> form resins only very slightly soluble in alcohol, which are also but slightly soluble in benzene, but which can be used in the manufacture of cellulose ester varnishes, being very soluble in ether, amyl acetate, ethyl acetate, etc. Finally, reference must be made to a process, according to which diarylacetal (i.e. alkylene diaryl ethers, such as  $CH_2(O \cdot C_2H_5)_2$  and  $CH_3 \cdot CH(O \cdot C_6H_5)_2$ , which are produced by interaction of the corresponding methylene chlorides with phenols, are condensed with formaldehyde.<sup>6</sup> According to the proportion of formaldehyde used, viscous oils, soft soluble resins or resins melting at a higher temperature and which are less soluble, and finally hardening resins, are produced. In consequence of the neutralization of the phenolic hydroxyl groups, such products show greater fastness to light than the

<sup>1</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 406,152 (1919); *Frdl.* XIV, 627; German Pat. 406,999 (1919); 407,000 (1920); *C.* (1925), I, 1816; *Kunstst.*, 15, 165 (1925); see also German Pat. 403,264 (1919); *C.* (1925), I, 307.

<sup>2</sup> Aktien-Ges. für Anilin-Fabrikation, German Pat. 358,399 (1920); *Frdl.* XIV, 624; *C.* (1922), IV, 956.

<sup>3</sup> Aktien-Ges. für Anilin-Fabrikation, German Pat. 358,400 (1920); *Frdl.* XIV, 625; *C.* (1922), IV, 956.

<sup>4</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 364,042 (1920); *C.* (1923), II, 913; *Frdl.* XIV, 625.

<sup>5</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 364,044 (1920); *C.* (1923), II, 922; *Frdl.* XIV, 1161; see also German Pat. 372,933 (1922); *Frdl.* XIV, 1162; *C.* (1923), IV, 602.

<sup>6</sup> Farb. vorm. Meister, Lucius & Brüning, A. Voss, German Pat. 397,315 (1922); *C.* (1924), II, 1412; *Frdl.* XIV, 1166; *Kunstst.*, 14, 156 (1924).

corresponding Novolaks and Resoles and their solubilities also differ, these products being insoluble in alkalis and soluble in alcohol, acetone, ether, aromatic hydrocarbons, chloroform, and especially in linseed oil.

Many variations in the solubility of the products can be effected by neutralization of the free hydroxyl groups of phenol-formaldehyde resins or of phenol-aldehyde resins in general, by alkyl, aralkyl or acyl groups.<sup>1</sup> The fastness to light and air are simultaneously improved. Generally speaking, such subsequent treatment of the phenol-aldehyde resins is too expensive<sup>2</sup> to allow the products to compete with natural resins or with other synthetic resins. The only exception is probably afforded by the use for this purpose of p-toluenesulphochloride, which is obtained in large quantity as a by-product of saccharine manufacture.<sup>3</sup> In addition, the preparation of the Albertol copals, described in the last section, may also be considered as a similar after-treatment, which is commercially possible.

A few processes must be mentioned<sup>4</sup> for producing

<sup>1</sup> A. Riebeck'sche Montanwerke A.-G., German Pat. 436,445, additional to 352,003, C. (1927), I, 190, recommend the treatment in alkaline solution with allyl or vinyl halides of the condensation products obtained in presence of acids from phenols and formaldehyde. Clear, viscous, transparent masses are obtained which easily dry or solidify in the air. Both the resulting classes of ether dissolve in alcohol or ether, but the allyl ethers only are soluble in benzene, and not the vinyl ethers.

<sup>2</sup> H. Bucherer, German Pat. 391,072 (1918); C. (1924), I, 2744; see also C. (1922), II, 704; (1923), II, 411; *Frdl.* XIV, 1151; German Pat. 399,677 (1919); C. (1924), II, 1520; German Pat. 400,639 (1919); C. (1925), I, 309; French Pat. 520,319 (1920); C. (1921), IV, 873; British Pat. 148,139, 148,366 (1920); C. (1922), II, 1222; M. Melamid, German Pat. 352,003 (1920); *Frdl.* XIV, 657; British Pat. 137,291-2-3 (1919); 143,185-7 (1920); C. (1921), IV, 1068; *Kunstst.*, 11, 6 (1921); C. (1922), IV, 157; Farb. vorm. Meister, Lucius & Brünig, German Pat. 372,933 (1922); C. (1923), IV, 602; *Frdl.* XIV, 1162; German Pat. 391,539 (1920); C. (1924), II, 1028; *Kunstst.*, 14, 139 (1924); I. G. Farbenindustrie A.-G., German Pat. 439,962; C. (1927), I, 1531.

<sup>3</sup> M. Jacobsohn, *Kunstst.*, 11, 105 (1921); W. Herzog, *Kunstst.*, 16.

<sup>4</sup> Collardon, German Pat. 274,875 (1913); C. (1914), II, 97; *Frdl.* XII, 861; *Kunstst.*, 4, 256 (1914); U.S. Pat. 1,105,619 (1914); Austrian Pat. 82,543 (1913); C. (1921), IV, 45 French Pat. 453,395 (1913); *Kunstst.*, 3, 463 (1913); Heine-mann, German Pat. 310,282 (1915); C. (1919), II, 266; *Frdl.* XIII, 969; British Pat. 11,394 (1914); U.S. Pat. 1,176,056 (1916); Austrian Pat. 82,489 (1915); C. (1921), IV, 45; Dutch Pat. 2,806; *Kunstst.*, 9, 123 (1919); Norwegian Pat. 33,016 (1920); Holzverkohlungs-Ind. A.-G., German Pat. 337,061 (1919); C. (1921), IV 219; *Kunstst.*, 11, 190 (1921); Aktien-Ges für Anilin-Fabrikation, German, Pat. 393,283 (1921); P. Horn, German Pat. 189,947 (1906); U.S. Pat. 898,476 (1908); Ellis, U.S. Pat. 944,420 (1919); Townsend, U.S. Pat. 1,273,954 (1918).



phenol-formaldehyde derivatives containing arsenic or mercury. Such substances are intended for use as antiseptic paints, anti-fouling compositions for ships' hulls, and also as seed disinfectants, and as protecting agents for crops in general.<sup>1</sup>

A further application of phenol-formaldehyde condensation products must be referred to which has already attained considerable technical importance; water-soluble derivatives of these and other similar substances are used as synthetic tanning agents.<sup>2</sup> The first product of this kind was produced by Stiasny,<sup>3</sup> by condensing formaldehyde with phenolsulphonic acids under very gentle conditions. He obtained a syrupy liquid, of slightly brownish colour, which dissolved in water to a pale and perfectly clear liquid. The syrupy or less concentrated liquids, which resemble natural liquid tannin extracts, are sold under the name of Neradol.<sup>4</sup> They show certain reactions for vegetable tannins, giving, for example, dark blue precipitates with ferric salts, and precipitates with gelatine solutions and with lead acetate. They form exceedingly effective tanning agents, which may be used either alone or in conjunction with natural tanning agents. The leathers obtained by their means are distinguished by their light colour.

Numerous processes for the production of synthetic tannins have been proposed.<sup>5</sup> The required solubility of the products

<sup>1</sup> F. Raschig, German Pat. 384,354 (1920).

<sup>2</sup> Grasser, *Synthetische Gerbstoffe, ihre Synthese, industrielle Darstellung und Verwendung*, Berlin (1920); A. Wagner, J. Paessler, *Handbuch für die gesamte Gerberei und Lederindustrie*, Leipzig (1925), pp. 679, 838, 849.

<sup>3</sup> German Pat. 262,558 (1911).

<sup>4</sup> These products are produced by the Badische Anilin- und Soda-Fabrik; Neradol D is obtained from phenolsulphonic acids and Neradol ND from naphthalenesulphonic acid (German Pat. 292,531).

<sup>5</sup> Badische Anilin- und Soda-Fabrik, German Pat. 260,379, 265,415, 266,124, 282,850, 291,457, 300,567, 301,451, 349,727, 358,126, 382,217, 388,680; British Pat. 189,190; Röhm & Haas, German Pat. 265,855, 265,915; Deutschkoloniale Gerb- und Farbstoffges. m.b.H., German Pat. 293,041-2, 293,640, 293,693, 293,866, 294,825, 303,640, 305,795, 306,132; vorm. Friedr. Bayer & Co., German Pat. 283,313, 409,783; Gesellschaft für Chemische Industrie in Basel, German Pat. 285,772; Fr. Hässler, German Pat. 328,340; J. R. Zink, German Pat. 344,033; 346,197; Chemische Fabriken Worms, German Pat. 368,521, 382,905, 386,469, 386,470, 392,461, 417,972; British Pat. 148,126, 148,897-9, 154,153, 154,162, 156,669, 156,670, 156,749, 157,851; Swiss Pat. 91,878; Elektrochemische Werke G.m.b.H., German Pat. 377,227, 379,026, 384,878, 386,012; Weiler-ter-Meer, German Pat. 383,189; Farbw. vorm. Meister, Lucius & Brüning, German Pat. 408,871, 423,033; A. Kämpf, German Pat. 436,446 (1923); H. M. Mc-Arthur & Co., Ltd., R. B. Croad, G. E.

in water is attained either by using sulphonated raw materials, or by subsequently sulphonating the condensation products. It may also be attained, for example, by the use of polyvalent phenols or by treatment with sulphites. The acidity due to the sulphonic acid groups is sometimes neutralized by alumina or chromium oxide, by which means exceptionally valuable tanning agents are stated to be obtained.

Apart from the Neradol products, the following synthetic tanning agents are used in the leather industry: "Ordoval" products and "Tannin F" of the Badische Anilin- und Soda-Fabrik; "Carbatan" products of Gerb- und Farbstoffwerke, H. Renner & Co.; "Corinal" of Chemische Fabrik Worms; "Ewol" of Elektrochemische Werke; "Esco" tanning extract of Chemische Fabrik, Jucker & Co., and many others.

Similar products have also recently been used as wetting agents in fur-dyeing and for textile finishing, such as "Leonil" for example.<sup>1</sup>

The condensation product of naphthalenesulphonic acid and formaldehyde has also been recommended as a de-rusting agent.<sup>2</sup>

## RESINS FROM PHENOLS AND OTHER ALDEHYDES

**Phenol-furfurol Resins.** The reaction between phenols and furfurol resembles that between phenols and formaldehyde, in so far as the former may also be carried to a stage at which insoluble, infusible products are formed, by prolonged heating, or hardening, of intermediate substances which are soluble and fusible. The phenol-furfurol resins are distinguished by the

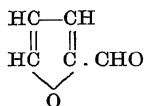
Knowles, U.S. Pat. 1,437,726, 1,443,697; British Pat. 182,823-4 (1921); A. Koetzle, British Pat. 141,714 (1920); 144,617 (1920); Chem. Fabriken und Asphaltwerke A.-G., British Pat. 156,254, 157,855-6; Gerb- und Farbstoffwerke H. Renner & Co. A.-G., British Pat. 171,729; W. Moeller, H. Renner British Pat. 148,750; W. Moeller, British Pat. 194,815; French Pat. 545,074, etc.

<sup>1</sup> On application as wetting agents for brake-bands, see British Dyestuffs Cor., Ltd., French Pat. 637,850: C. (1928). II, 2207.

<sup>2</sup> Zoellner-Werke A.-G., German Pat. 466,077; *Farben-Ztg.*, 34, 215 (1928-29).

fact that they are only obtainable of a dark or black colour, for which reason their use is restricted.<sup>1</sup>

Furfural (fural,  $\alpha$ -furane-aldehyde),  $C_5H_4O \cdot CHO$ , has the constitution—



It is a colourless liquid, which rapidly turns brown in the air, of boiling point  $161-161.5^\circ C.$ , and specific gravity  $d_{20} 1.1594$ , soluble in 11 parts of water. It is produced by the decomposition of pentoses and indirectly from many carbohydrates, for example, by the action of dilute acids. Recently, in the United States the production of furfural has been made very much less costly by the use of maize cobs and oat bran as raw materials, a yield of about 6 per cent of the weight of the raw material being obtained.<sup>2</sup>

Being an aldehyde, furfural easily undergoes condensation, for example with phenols, but its character as a furfurane derivative is also manifested by its considerable tendency to polymerization, in which it resembles cumarone. This tendency is the explanation of the formation of infusible, insoluble masses if the reaction is carried sufficiently far. This circumstance also explains the peculiar action of acid condensing agents, which greatly accelerate the polymerization of the condensation products which are formed, similarly to their action in the formation of cumarone resin, whilst alkalis are less active in this respect. Phenol-furfural resins are thus, in a sense, provided with resinophoric groups from the commencement, whereas in the case of phenol-formaldehyde resins it must be assumed that these are formed in the course of the

<sup>1</sup> On the use of such resins for the production of black phenolformaldehyde resins, see Bakelite Cor., Cl. A. Nash, U.S. Pat. 1,524,995 (1924); *C.* (1925), I, 2261. See also Urbanus, *Kunstst.*, 17, 29, 86, 108 (1927).

<sup>2</sup> Mains, *Chem. Met. Eng.*, 26, 779, 841 (1922); Roger Adams, Kamm, Marvel, *J. Ind. Eng. Chem.*, 13, 133 (1921); U.S. Pat. 1,357,467; Mains, Phillips, *Chem. Met. Eng. Chem.*, 24, 661 (1921); Miner, Trickey, Brownlee, *idem.*, 27, 363 (1922); *The Miner Laboratories Bulletin*, No. 2 (1925); *Chem. Met. Eng.*, 27, 300 (1922).

condensation only. This may account for the fact that furfural-alcohol may be used instead of furfurol itself.<sup>1</sup>

The resinification of phenols with furfurol has been known for a long time,<sup>2</sup> but was first investigated more closely by Beckmann and Dehn,<sup>3</sup> who arrived at the following results as a result of many variations of the experimental conditions.

The reaction velocity is largely dependent on the quality and quantity of the condensing agent and on the character of the phenol. The character of the final product depends largely on the proportions of the two components.

If concentrated hydrochloric acid is added to a solution of phenol and furfurol, a reddish-violet colour first appears, which soon changes to deep blue. The mixture becomes hot and, finally, solidifies to a hard black product which is not attacked by acids or alkalies, and is insoluble in such solvents as alcohol, chloroform, acetone and benzene. The product, which is approximately of the same hardness as Bakelite C, possesses a certain degree of elasticity.

On varying the proportions of the components it is found that a mixture of equal parts of phenol and furfurol solidifies most rapidly, forming the end-product just described. In the presence of hydrochloric acid a fusible, non-hardening product, soluble in both acetone and alcohol, could only be obtained when not more than 10 to 20 per cent of furfurol was present, calculated on the phenol, and the excess of phenol finally distilled off.

The concentration of the hydrochloric acid affects the reaction-velocity very greatly. Whilst a mixture of equal parts of phenol and furfurol, to which about 0.7 per cent of concentrated hydrochloric acid had been added, stood for three weeks before solidifying, and only hardened further very slowly, these phenomena took place very much more rapidly if  $2\frac{1}{2}$  per cent or more of acid was added. Thus, when 5 or 10 per cent were

<sup>1</sup> Quaker Oats Co., J. P. Trickey, C. S. Miner, U.S. Pat. 1,665,235-6-7; C. (1928), II, 816.

<sup>2</sup> Perioz, *Wagners Jahresberichte* (1860), 487; Stenhouse, *Proc. Roy. Soc.*, 18, 537 (1870); Claisen, *Ann.*, 237, 272 (1887).

<sup>3</sup> *Sitzungsber. Kgl. Preuss. Akad. Wiss.*, Berlin (1918), 1201; C. (1919), I, 440.

added solidification occurred within one hour, and the product became quite hard within one day.

Alcoholic or gaseous hydrochloric acid, sulphuric acid,<sup>1</sup> and phosphoric acid behave similarly to a strong, aqueous hydrochloric acid. On the contrary, organic acids, such as acetic, tartaric, benzoic and oxalic acids, influence the condensation but slightly, even on prolonged heating.<sup>2</sup> Aniline hydrochloride and hydroxylamine hydrochloride are effective, whilst ammonium chloride does not induce the reaction to proceed to the final product. Organic halogen compounds which liberate halogen hydride, such as acid chlorides, epichlorhydrin, acetylene tetrachloride and carbon tetrachloride are also recommended.<sup>3</sup> According to Beckmann and Dehn, metallic chlorides of zinc and aluminium, also have an accelerating effect. Lead acetate, the iron salt of pyromucic acid,<sup>4</sup> and finely-divided metals<sup>5</sup> may also be used. The reaction may also be assisted by working under pressure.

Basic condensing agents act in a manner essentially different from that of acids. Whilst the use of acids leads directly to the formation of the end-products, stable intermediate products of soluble, fusible but hardening character can conveniently be obtained by basic condensing agents;<sup>6</sup> the extremely slow course of the reaction in this case is, however, very noticeable compared with the rapidity of the phenol-formaldehyde condensation under similar conditions. Thus, mixtures of equal parts of furfural and phenol or cresol, in presence of 10 per cent of powdered sodium or potassium carbonate, require to be heated for three hours to 100° C. before forming a solid, brown rubber-like mass, which dissolves in alcohol or benzene to form a clear varnish, and which is converted into the insoluble,

<sup>1</sup> Steinitzer, German Pat. 305,624 (1917); *Kunstst.*, 10, 10 (1920).

<sup>2</sup> Trickey, Miner, Brownlee, *J. Ind. Eng. Chem.*, 15, 05; *C.* (1923), IV, 211.

<sup>3</sup> Bakelite Ges. m.b.H., Swiss Pat. 85,076; 86,308; *Kunstst.*, 11, 62 (1921); *C.* (1920), II, 495; Austrian Pat. 86,764; *C.* (1922), IV, 714.

<sup>4</sup> Quaker Oats Co., J. P. Trickey, C. S. Miner, U.S. Pat. 1,665,233; *C.* (1928), II, 815.

<sup>5</sup> Quaker Oats Co., J. P. Trickey, C. S. Miner, U.S. Pat. 1,665,234; *C.* (1928), II, 815.

<sup>6</sup> Basic salts may also be used; Meunier, French Pat. 23,821, addition to French Pat. 472,384; *C.* (1922), IV, 800; *Kunstst.*, 12, 164 (1922); Meunier, *Rev. chim. ind.*, 32, 103; *C.* (1923), IV, 113.

infusible condition on further heating. It is interesting to note that in contrast to this behaviour of phenol and to that of  $\beta$ -naphthol,  $\alpha$ -naphthol shows an exceptional reactivity in this case. According to Trickey, Miner and Brownlee, a proportion of about 1.25 mol. furfural to 1 mol. phenol is advisable for the production of insoluble resins by alkaline condensation.

Phenol-furfural resins have been recommended for the production of press-mouldings, for impregnating paper, and so forth.<sup>1</sup> It is stated that they are exceptionally suitable for cold moulding.<sup>2</sup> It appears that furfural is only commonly used in conjunction with formaldehyde, either by adding formaldehyde, hexamethylene tetramine, and so forth, to phenol-furfural resins in order that they may be more easily hardened, or conversely, by the addition of furfural as an after-treatment of phenol-formaldehyde resins or other condensation products (for example with acetaldehyde).<sup>3,4</sup> According to Stokes, deep black, lustrous resins so produced are especially used for the manufacture of gramophone discs and printing matrices.

**Phenol-acrolein Resins.** The condensation products of acrolein with phenols can be hardened, just as can those from furfural and phenols, i.e. they can be converted by heating into an insoluble and infusible condition. In this case also the cause of the hardening process is the tendency to polymerization, which is strongly marked in uncombined acrolein (see page 84 *et seq.*), that is to the terminal vinyl group.

The production and utilization of such resins proceeds in an exactly analogous manner to that of the phenol-formaldehyde

<sup>1</sup> See Novotny, U.S. Pat. 1,377,519 (1921); printing plates: U.S. Pat. 1,398,148 (1921); gramophone discs: U.S. Pat. 1,398,147 (1921).

<sup>2</sup> The stickiness of the resins is stated to be overcome by the addition of zinc stearate or aluminium palmitate; see C. Ellis, T. S. Huxham, U.S. Pat. 1,571,447 (1922); *C.* (1926), I, 2854.

<sup>3</sup> Novotny, Kendall, U.S. Pat. 1,398,146 (1921); J. S. Stokes, British Pat. 243,470 (1924); *C.* (1926), II, 1595.

<sup>4</sup> Felten & Guillaume Carlswerk Akt.-Ges., German Pat. 363,917 (1919); 365,626 (1920); *C.* (1923), II, 257, 754; *Kunstst.*, 13, 70 (1923); H. O. Keay, Canadian Pat. 245,798 (1924); *C.* (1926), I, 210, grinding discs; Plausons Forschungsinstitut G.m.b.H., German Pat. 352,521 (1920); *Kunstst.*, 12, 133 (1922), on hardening natural and synthetic resins; C. Ellis, U.S. Pat. 1,592,296 (1922); 1,592,773 (1923); *C.* (1926), II, 1594, on the after-treatment of phenol-acetaldehyde and butyraldehyde resins.

resins, the components being heated together in presence of substances of alkaline reaction,<sup>1</sup> or in the presence of condensing agents generally,<sup>2</sup> until a soluble initial condensation product is formed or until the end-product is produced. The polymers of acrolein, which are obtainable by the action on acrolein of small quantities of alkali, may be used instead of acrolein itself. The end-products are insoluble, infusible masses, of yellowish to brown colour, which cannot be scratched and are bad conductors of electricity, for which reason their use has been recommended for the production of objects required by the electrical industry.

**Phenol-acetaldehyde Resins.** Acetaldehyde behaves in an essentially dissimilar manner from formaldehyde and the other aldehydes mentioned above (furfural and acrolein), as on condensation with phenols it forms soluble, fusible and non-hardening resins only. These products are distinguished by solubility in benzene hydrocarbons and miscibility with fatty oils, but the character of the products is not altogether satisfactory, especially with regard to colour.

The fact that resins are formed by the action of acetaldehyde on phenols (phenol, pyrogallol),<sup>3</sup> naphthols,<sup>4</sup> resorcinol,<sup>5</sup> and so forth, in the presence of acid condensing agents, such as sulphuric acid;<sup>3</sup> and hydrochloric acid<sup>4</sup> was discovered by Baeyer in 1872,<sup>3</sup> and was then investigated in detail by Claus and Trainer,<sup>4</sup> and by Michael and Comey.<sup>5</sup> (See page 178 *et seq.*) The technical exploitation of the products was first suggested by Smith,<sup>6</sup> who proposed to use the resin obtained in alcoholic solution by means of hydrochloric acid or sulphur dioxide, for the production of a substitute for ebonite and wood and as an insulating material. As is well known,

<sup>1</sup> Ch. Moureu, Ch. Dufraisse, German Pat. 382,903 (1920); *C.* (1924), I, 1715; British Pat. 141,059 (1920); *Kunstst.*, 10, 183 (1920); see also British Pat. 141,058 (1920); French Pat. 528,498 (1920); *Kunstst.*, 12, 164 (1922).

<sup>2</sup> J. McIntosh, E. Yeakle, Canadian Pat. 229,397 (1922); *C.* (1924), I, 1717; *Kunstst.*, 14, 71 (1924).

<sup>3</sup> *Ber.*, 5, 25, 280, 1094 (1872); Fabinyi, *Ber.*, 11, 283 (1878).

<sup>4</sup> *Ber.*, 19, 3004 (1886).

<sup>5</sup> *Am. Chem. Journ.*, 5, 349 (1883-4); in this article the use of alkaline condensing agents is also mentioned.

<sup>6</sup> A. Smith, German Pat. 112,685 (1899); *Chem. Ztg.* (1900), 740; British Pat. 16,247 (1899); U.S. Pat. 643,012 (1900).

phenol-formaldehyde resins have proved far better for such purposes. The acetaldehyde products can be endowed with a certain degree of hardening capacity if the condensate with phenols is subsequently treated with formaldehyde, hexamethylene-tetramine, or similar agents.<sup>1</sup>

Acids are the condensing agents mainly used for the reaction between phenols and acetaldehyde.<sup>2</sup> As the one component, the acetaldehyde, is a very volatile substance, the reaction, which proceeds very violently in presence of condensing agents, must be retarded by suitable means, or otherwise so effected that no losses occur. This may be secured by the gradual addition of paraldehyde, for example,<sup>3</sup> and by allowing to stand for some time after each addition, after which the batch is heated for a short time to 150° C. According to other processes the aldehyde is introduced in the gaseous condition, in which case it is found advantageous to dilute it with inert gases, such as nitrogen or carbon dioxide,<sup>4</sup> in order to be able to control the reaction. It is also stated that the reaction may be carried to an exceptionally advanced stage in the presence of organic solvents, such as carbon tetrachloride, trichlorethylene, and so forth,<sup>5</sup> in which case softening points of 75–95° C. and over are alleged to be attained. The proposal has also been made to carry out the reaction in an autoclave in an atmosphere of compressed inert gas, such as nitrogen.<sup>6</sup> After the reaction has been effected in one manner or another

<sup>1</sup> B. Bakelite, Ges. m.b.H., German Pat. 375,638 (1918); *C.* (1923), IV, 602; Swiss Pat. 87,893; Canadian Pat. 228,557; U.S. Pat. 1,598,546; Potter, Fleet, Damard Laquer Co., Ltd., British Pat. 169,347 (1920); *C.* (1922), IV, 381; *Kunstst.*, 13, 21 (1923); D. S. Kendall, Condensite Co., British Pat. 159,164 (1920); *C.* (1921), IV, 45; Canadian Pat. 232,251; and others.

<sup>2</sup> Bases and acid or basic salts have also been recommended: Bakelite G.m.b.H., German Pat. 375,638 (1918); *C.* (1923), IV, 602; Swiss Pat. 87,893 (1919), additional to 85,572; *C.* (1921), IV, 269; *Kunstst.*, 11, 15, 47 (1921); Canadian Pat. 228,557 (1922); *C.* (1924), I, 517.

<sup>3</sup> C. Ellis, U.S. Pat. 1,500,303 (1923); *C.* (1926), II, 1470; *Kunstst.*, 16, 254 (1926).

<sup>4</sup> Progress A.-G., German Pat. 426,866 (1923); *C.* (1926), II, 1206.

<sup>5</sup> Farb. vorm. Meister, Lucius & Brünig, German Pat. 365,286 (1920); *Frdl.* XIV, 1183; *C.* (1923), II, 922.

<sup>6</sup> Canadian Electro Products Co., Ltd., U.S. Pat. 1,653,302; *C.* (1928), II, 815; HCl, chlorides of sulphur, chlorides of phosphorus, and chlorides of organic acids are described as condensing agents, in quantities up to 10%.



it is completed by heating for some time, after which the condensing agent is neutralized if necessary, and the uncombined raw materials and water of reaction are removed by distillation in a vacuum or in a current of steam.

In place of actual acetaldehyde, or its polymers, the use of nascent acetaldehyde has been suggested, by leading acetylene into a solution of the phenol, to which mercury salts and acids are added.<sup>1</sup>

For example, mercuric oxide is dissolved in 30 per cent sulphuric acid, crude phenol or cresol is added, and acetylene led into the liquid with vigorous stirring. After absorption is complete the viscous reaction product is separated from the aqueous solution and washed, after which the excess of phenols is expelled in a current of steam. The resinous condensation product may be freed from mercury by dissolving in alcohol or benzene.

The resins obtained in this way from acetylene and phenols may be converted into harder products of higher melting point<sup>2</sup> by treatment with aldehydes, such as acetaldehyde, or even into insoluble and infusible products, with formaldehyde or its equivalents.<sup>3</sup>

Similar products are presumably formed by a process consisting in acting with alkaline reagents on wood distillation products, which are well known to contain both aldehydes and phenols.<sup>4</sup> The acid oils, containing phenols, from lignite tar

<sup>1</sup> Chem. Fabrik Güstrow, Dr. Hillringhaus & Dr. Heilmann, German Pat. 422,904 (1914); *C.* (1926), I, 2852; Melamid, British Pat. 163,679 (1920). *C.* (1921), IV, 838; French Pat. 527,112; *C.* (1922), II, 660; Norwegian Pat. 33,965 (1920); *Kunstst.*, 12, 165 (1922); see also Consortium für elektrochem. Ind. G.m.b.H., French Pat. 593,338 (1925); Austrian Pat. 103,106 (1925); *C.* (1926), II, 1791; J. A. Nieuwland, British Pat. 183,830; *C.* (1923), IV, 951; *Kunstst.*, 13, 125 (1923); on the course of the reaction, which is quite analogous with that with acetaldehyde, see H. H. Wenzke, J. A. Nieuwland, *J. Am. Chem. Soc.*, 46, 177; *C.* (1924), I, 1031.

<sup>2</sup> J. S. Stokes, E. E. Novotny, D. S. Kendall, U.S. Pat. 1,470,637 (1922); *C.* (1926) II, 1469; *Kunstst.*, 16, 254 (1926).

<sup>3</sup> Canadian Electro Products Co., Ltd., H. W. Matheson, Canadian Pat. 239,863 (1922); British Pat. 227,216 (1923); *C.* (1926), II, 1472; *Kunstst.*, 16, 255 (1926); the same and F. W. Skirrow, Canadian Pat. 250,294 (1922); British Pat. 232,277 (1923); *C.* (1926), II, 1473; *Kunstst.*, 16, 231 (1926).

<sup>4</sup> P. Camus & Co., P. Bardy, German Pat. 234,806 (1908); *Frdl.* X, 1058; *C.* (1911), II, 118; *Kunstst.*, 2, 165 (1912); British Pat. 402,907 (1908); see R. P. Duchemin, *Bull. Soc. Chim.* (4), 7, 473; *C.* (1910), II, 604.

and low temperature tar have also been subjected to the action of acetaldehyde, oil-soluble resins being so obtained.<sup>1</sup> Oil-soluble products are also formed with  $\alpha$ -tetrahydronaphthols.<sup>2</sup>

Improved products, showing better solubility in linseed oil, are stated to be obtained by the condensation of phenol-acetaldehyde resins with natural resins, such as colophony,<sup>3</sup> a reaction similar to the familiar method of production of the Albertols, but which results in no such decisive improvement in the solubility, as the original products are already soluble in benzene and in oil.

The production of phenol-acetaldehyde resins has also been developed in another direction, namely, by replacing the very volatile acetaldehyde or its polymers by the condensation products of acetaldehyde, aldol and crotonaldehyde. In the presence or absence of condensing agents these interact with phenols,<sup>4</sup> or with partially etherified polyvalent phenols,<sup>5</sup> to form oily linseed oil substitutes or resinous products. In order to obtain products more resistant to heat, the recommendation has been made to carry out the condensation in the presence of water and mineral acid.<sup>6</sup> The soluble and fusible products so obtained become insoluble and infusible by subsequent treatment with formaldehyde.<sup>7</sup> The solubility and elasticity of the soluble and fusible products can be improved by effecting the condensation in the presence of natural resins, or by subsequently melting them together with these.<sup>8</sup> Finally,

<sup>1</sup> Chem. Fabr. Worms, British Pat. 156,740 (1921); *C.* (1921), II, 808.

<sup>2</sup> Akt.-Ges für Anilin-Fabrikation, German Pat. 356,224 (1918); *Frdl.* XIII, 1119.

<sup>3</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 374,379 (1920); *Frdl.* XIV, 1185; German Pat. 376,729 (1921); *Frdl.* XIV, 1186.

<sup>4</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 364,041 (1920); *Frdl.* XIV, 1173; *C.* (1923), II, 921.

<sup>5</sup> Farb. vorm. Meister, Lucius & Brüning, German Pat. 364,043 (1920); *Frdl.* XIV, 1174; *C.* (1923), II, 921.

<sup>6</sup> Farb. vorm. Meister, Lucius & Brüning, G. Balle, H. Wohlers, German Pat. 406,153 (1922); *C.* (1925), I, 1817; *Frdl.* XIV, 1179; *Kunstst.*, 15, 165 (1925).

<sup>7</sup> Farb. vorm. Meister, Lucius & Brüning, G. Balle, German Pat. 388,792 (1921); the same and A. Steindorff, German Pat. 388,795 (1922); *C.* (1924), II, 550; *Kunstst.*, 14, 139 (1924); *Frdl.* XIV, 1175, 1176.

<sup>8</sup> Farb. vorm. Meister, Lucius & Brüning, A. Steindorff, F. Giloy, G. Balle, H. E. Wohlers, German Pat. 388,794 (1922); *C.* (1924), II, 551; *Frdl.* XIV, 1177; *Kunstst.*, 14, 139 (1924).

the products can be endowed with solubility in dilute alkalis by interaction with monochloroacetic acid, a modification which should make them suitable for use as shellac substitutes for certain textile finishing operations.<sup>1</sup>

Phenol-acetaldehyde resins, in the wider sense, have been recommended for use as varnish primings, as impregnating agents, as adhesives for the production of printing matrices, panelling, etc.<sup>2,3</sup> On the addition of hexamethylene-tetramine to a solution of phenol-acetaldehyde resin for the production of a hardening binding medium, for use in the manufacture of laminated products similar to hardened paper, see Novotny.<sup>4</sup> Resinous products which are especially suitable for cold press-moulding have been described by C. Ellis.<sup>5</sup>

**Resins from Phenols and other Aldehydes or Ketones.** In the main the synthetic resins obtained by condensing phenols with other aldehydes or with ketones closely resemble those obtained with acetaldehyde. They differ from resoles by the absence of any well defined capacity for being hardened, which can only be imparted to some extent by subsequent treatment with substances such as formaldehyde, hexamethylene-tetramine, and furfural. The products are also more universally soluble than the resoles in organic solvents, being most of them soluble not only in alcohol, but also in benzene, fatty oils, and so forth. The resins belonging to this class are of but little practical importance, if only an account of the high cost of the aldehydic or ketonic components.

The condensation of phenols with butyraldehyde in the presence of acid condensing agents has been dealt with by C. Ellis.<sup>6</sup> The resultant resins are intended for use in varnishes

<sup>1</sup> Farbw. vorm. Meister, Lucius & Brüning, G. Balle, German Pat. 388,793 (1922); *C.* (1924), II, 551; *Kunstst.*, 14, 139 (1924); *Frdl.* XIV, 1178; I. G. Farbenindustrie A.-G., German Pat. 439,962; *C.* (1927), I, 1531.

<sup>2</sup> J. S. Stokes, British Pat. 176,828 (1920); *C.* (1922), IV, 638; *Kunstst.*, 12, 154 (1922).

<sup>3</sup> On the production of drying agents, see H. Rauch, German Pat. 402,539 (1922); *Kunstst.*, 15, 12 (1925).

<sup>4</sup> U.S. Pat. 1,440,097 (1922).

<sup>5</sup> U.S. Pat. 1,645,693; *C.* (1928), II, 815.

<sup>6</sup> U.S. Pat. 1,477,870 (1922); *C.* (1926), II, 1470; *Kunstst.*, 16, 254 (1926); see also Bakelite Cor., U.S. Pat. 1,667,872; *C.* (1928), II, 815.

and as adhesives. The interaction of tiglic aldehyde with guaiacol, cresol and pyrogallol-dimethylether was investigated by Doebner<sup>1</sup> in view of the probable constitution of guaiacum resin as a condensation product of phenols with aldehydes. A shellac substitute is stated to be produced by the condensation of phenols with glyoxal.<sup>2</sup>

Among aromatic aldehydes, benzaldehyde has been studied particularly closely with regard to its condensation products with phenols. Thus, von Baeyer<sup>3</sup> already obtained resinous substances from benzaldehyde and pyrogallol or resorcin in the presence of hydrochloric acid or strong sulphuric acid. The reaction was more closely studied later by Michael,<sup>4</sup> who included phenol and salicylic aldehyde in his investigations. Further attention was also devoted to the effect of variations in the character and quantity of the condensing agent. It is of interest to note that these resins become brown in the air in consequence of oxidation, a difficulty which is particularly marked when condensation is effected in an alkaline medium. Among new developments regarding the production of substances of this character, it has been found that benzal chloride can be condensed with phenols in the presence of small amounts of ferric chloride.<sup>5</sup> It has been found that benzotrichloride can also be used, and also toluenes which are chlorinated in the side chain.<sup>6</sup>

In patent specifications the use of ketones instead of aldehydes for condensation with ketones is sometimes recommended. The reaction occurs in a similar manner to that with aldehydes. Thus,<sup>7</sup> from 2 mol. phenol and 1 mol. acetone in

<sup>1</sup> *Arch. Pharm.*, 234, 610 (1896); *C.* (1897), I, 167.

<sup>2</sup> Weiler-ter-Meer, German Pat. 362,381 (1919); *Frdl.* XIV, 1195.

<sup>3</sup> *Ber.* 5, 25, 280, 1094 (1872).

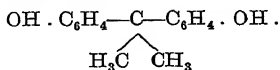
<sup>4</sup> *Am. Chem. Journ.*, 5, 338 (1883-4).

<sup>5</sup> Dynamit A.-G., vorm. A. Nobel & Co., German Pat. 355,389 (1920); *Frdl.* XIV, 1199. See also the investigations of Gluud and Breuer, *Ges. Abhandlungen zur Kenntnis der Kohle*, 4, 221 (1919-1920); *C.* (1921), II, 855; Phenol or Cresols with Benzaldehyde: Beckmann, Dehn, *Sitzungsber. Kgl. Preuss Akad. Wiss.*, Berlin (1918), 1201; *C.* (1919), I, 440; Phenol, Furfurol and Benzaldehyde, etc. On resin production from hydrobenzamide and phenol, see Karpen & Bros., British Pat. 9,292 (1914).

<sup>6</sup> Ellis-Foster Co., U.S. Pat. 1,648,852; *C.* (1928), II, 814.

<sup>7</sup> Zincke, *Ann.*, 343, 85 (1905); *Ann.*, 388, 299 (1912); 400, 33 (1913).

hydrochloric acid solution, the crystalline product p-dihydroxydiphenyl- $\beta$ - $\beta'$ -propane is formed—



Corresponding products are also obtained with cresols, but in general such products show a very decided tendency to crystallization. Therefore condensation products from phenols and ketones are usually only recommended for the production of resinous materials either in the simultaneous presence of aldehydes, or with subsequent treatment with aldehydes, and especially with formaldehyde, which substance also confers hardening properties on the product.<sup>1</sup>

The same principle underlies the process of Chemische Fabrik, Dr. Kurt Albert, C.m.b.H., which is carried out in a similar manner to the process of the same firm for the treatment of phenol-formaldehyde resin. (See page 327.) The product first obtained from phenols and ketones, for example, under the influence of hydrochloric acid, is subsequently treated with formaldehyde in alkaline solution.<sup>2</sup>

Condensations of cyclic ketones with phenols or their hydrogenated derivatives result in the production of resins which are more particularly intended for additions to other products, such as resins, cellulose products and rubber.<sup>3</sup> Mixtures of cyclic ketones, such as cyclohexanone, with phenols may be caused to interact with aldehydes of various kinds to form various resinous products, some of which are soluble in linseed oil.<sup>4</sup>

Resins soluble in weak alkalis can be obtained by the condensation of aldehydecarboxylic acids or ketonecarboxylic acids

<sup>1</sup> Beatty, U.S. Pat. 1,113,926 (1914); 1,158,962 (1915); 1,225,748-9; 1,225,750 (1917); *Kunstst.*, 8, 9 (1918); French Pat. 447,647 (1912); British Pat. 18,824 ((1912); *Kunstst.*, 4, 76 (1914); Austrian Pat. 67,693; *Kunstst.*, 5, 130 (1915); Belgian Pat. 252,592; *Kunstst.*, 3, 275 (1913); Intosh, U.S. Pat. 1,448,556; *Kunstst.*, 14, 44 (1924); 16, 254 (1926); *C.* (1926), II, 1468; Terwilliger, British Pat. 218,277, 218,638 (1924); French Pat. 583,582 (1924); *C.* (1926), II, 1474, etc.

<sup>2</sup> U.S. Pat. 1,614,172; British Pat. 261,522; French Pat. 596,071; *C.* (1927), I, 1891.

<sup>3</sup> Y. Johnson, British Pat. 276,518.

<sup>4</sup> Badische Anilin- und Soda-Fabrik, O. Schmidt, K. Seydel, German Pat. 407,668 (1922); *C.* (1925), I, 1818; *Kunstst.*, 15, 165 (1925); *Frdl.* XIV, 1182.

with phenols.<sup>1</sup> On the other hand, condensation products of phenols with aldehydes other than formaldehyde, which are insoluble in alkali, can be obtained by neutralizing the free hydroxyl groups by the attachment of alkyl or acyl groups.<sup>2</sup>

### DETECTION AND INVESTIGATION OF PHENOL ALDEHYDE RESINS

This section deals primarily with the resins obtainable from phenols and formaldehyde, which are of far greater importance than the other similar products. The methods described are, however, directly applicable to the other resins.

**Detection.** Phenol-formaldehyde resins, and especially the hardened products, can be identified by the circumstance that they liberate considerable quantities of free phenols on decomposition. Thus, many such resins liberate sufficient quantities of phenols for identification on heating with strong caustic soda solution, and all on heating strongly with soda-lime.<sup>3</sup> A considerable quantity of phenols is liberated by dry distillation only, so that this method is preferable.<sup>4</sup>

The sample to be investigated is finely powdered and heated in a retort or distilling flask in a current of nitrogen, the vapours being condensed. The distillate may conveniently be led almost to the bottom of a conical flask by a suitably bent tube; the flask is provided with a stopper and with an outlet tube which acts as an air cooler. In this manner the following proportions of phenol were obtained from commercial samples of known origin—

From Juvelith	.	.	.	17.8%	phenol
Resan	.	.	.	20.5%	"
Dekorite				24.2%	"
Faturan				21.7	

With regard to the origin of the phenol which is so liberated, Herzog states that it is probably loosely combined in the resin in the form of phenyl-ether,  $-\text{O} \cdot \text{C}_6\text{H}_5$ .

<sup>1</sup> Farbzw. vorm. Meister, Lucius & Brüning, German Pat. 362,382 (1920); C. (1923), II, 920; *Frdl.* XIV, 1160.

<sup>2</sup> H. Bucherer, German Pat. 399,677 (1919); *Frdl.* XIV, 1155.

<sup>3</sup> Steinitzer, *Kunstst.*, 5, 109 (1915).

<sup>4</sup> W. Herzog, *Angew.*, 34, 97, 159; C. (1921), II, 1067; IV, 195.

The identification of the phenols so liberated offers no difficulties, and in this way the nature of the phenolic component of a given phenoplast can readily be ascertained.

**Investigation.** When testing phenol-formaldehyde resins it must be recognized that very various products have to be distinguished, for example, hardening and non-hardening resins, and varieties soluble in acetone, spirit, and so forth, or soluble in oil, and that the requirements vary greatly from case to case according to the intended application.

**Appearance and Odour.** The solid phenol-formaldehyde resins are sold almost exclusively in lump form and only seldom as powders. They form transparent masses of the same character as natural resins, but should offer the advantage of being free from impurities. Recently, success has been achieved in producing all these products, i.e. the Novolaks, the oil-soluble and the hardened products, free from phenol and, therefore, in practically odourless form. Whilst complete freedom from odour should be insisted on in the case of resins intended for varnish production, this is not necessarily the case for hardening resins, for which this condition is often waived, thus enabling cheaper products, containing free phenol, to be used.

The liquid phenol-formaldehyde resins are more or less viscous substances, which are also obtainable in odourless qualities. They are capable of being hardened. They become more viscous on storage, for which reason, if importance is attached to the maintenance of uniform working conditions, viscosity determinations are necessary, for which the well-known falling sphere viscometer is especially suitable.<sup>1</sup>

**Colour and Fastness to Light.** Phenol-formaldehyde resins are usually pale brown to dark brown in colour, but certain qualities of the Novolak and oil-soluble types, used for preparing varnishes, are supplied in qualities which are quite pale or colourless. In connection with the oil-soluble Albertol copals, an exact method of indicating the depth of colour has been evolved by Fonrobert and Pallaud,<sup>2</sup> the use of which may be

<sup>1</sup> Regarding this, see J. Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), pp. 479 *et seq.*

<sup>2</sup> *Farbenztg.*, 31, 967, 1354 (1926).

recommended in other cases in which the colour affects the value of a resin product. The depth of colour is measured by comparison with that of a solution of iodine in aqueous potassium iodide, and is indicated by a so-called colour index, which is defined as follows.

“The colour index (F.Z.) of a resin or other product indicates the number of milligrams of free iodine in 100 c.c. of an aqueous iodine-potassium iodide solution of the same depth of colour, whereby the sample under examination is observed in the form of a layer of 10 mm. thickness.”

The colour intensities of the sample and iodine solution are always compared by transmitted light, and this may be done in similar test-tubes of 10 mm. bore, the iodine solution being diluted with distilled water until the colour intensities are equal and the contents of free iodine in 100 c.c. of the solution then determined by titration in the ordinary manner. By the preparation of a colour scale of iodine solutions of known concentration the titration of the iodine in each individual case is rendered unnecessary.

The colour intensity may also be determined by varying the depth of the comparative solution, for example, until the sample and the comparative solution appear to be of the same colour intensity by transmitted light. For this purpose colorimeters are suitable, which enable the depth of the layers to be determined directly.<sup>1</sup> In this method the assumption is made that the depth of colour is proportional to the depth of the liquid. As this is not the case for linseed oil, varnishes, resins, and so forth, Fonrobert and Pallauf recommend that such materials should be examined in a layer 10 mm. thick, and that the height of the iodine solution should be varied, as this latter corresponds to the above-mentioned assumption, it being recognized that its colour intensity varies proportionally to the iodine concentration. The colour index can then be calculated from the iodine contents of the solution in milligrams per 100 c.c. (G), the depth of the iodine solution millimetres ( $H_i$ ), and the

<sup>1</sup> On Hellige's colorimeter see Ubbelohde, *Petr.*, 10, p. 275 (1914-15); on the colorimeters of Duboscq and others, see *J. Ind. Eng. Chem.*, 14, 269, 274 (1922).



depth of the layer of the sample in millimetres ( $H_s$ ), which latter should be as nearly as possible, 10, from the following formula—

$$\text{Colour index} = \frac{H_i}{H_s} G.$$

Fonrobert and Pallauf have constructed an apparatus<sup>1</sup> for rapid determination by this method with an accuracy of about 5 per cent, in which the variations in the depth of the comparative layer are effected by means of a set of hollow glass prisms (so-called indigo prisms), which are interchangeable and movable across an observation slit. The prisms are provided with scales and are filled with standard iodine solutions, containing, for example, 4, 16, 64, and 256 mg. of free iodine per 100 c.c. In completely filled bottles or prisms such solutions remain practically unchanged, and those only containing less than 4 mg. of iodine per 100 c.c. need to be tested from time to time and replaced if necessary.

According to Fonrobert and Pallauf, iodine solutions of this kind are exceptionally suitable for these colorimetric determinations as their shade corresponds "in a quite ideal manner" to that of colophony, most natural and synthetic resins, varnishes, oils, and so forth.

Resins can be tested for fastness to light in a very effective manner by exposing their concentrated solutions in spirit to a light source, and measuring the colour index from time to time. Similar investigations can, of course, be carried out with the solid resins and with films.

**Melting and Softening Points.** Phenol-formaldehyde resins intended for varnishes should possess the highest possible melting and setting points, whilst the hardening qualities need only exceed certain lower limits of melting point of about 50° C.; this is of importance, so that failure of the reaction to proceed up to a certain point may be detectable. The determination of the melting and softening points of non-hardening resins is effected by the methods used for resins in general. A sample is heated in a melting point capillary in a bath of sulphuric acid, and the temperatures are noted of initial sintering, melting, and clarifying. (See Albertol Copals.) A similar melting

<sup>1</sup> Obtainable from C. Desaga, Heidelberg.

point determination may also be made on hardening resins, but in the case of these the determination of the softening point by the method of Kraemer and Sarnow, which is usually employed for resins, encounters difficulties, as these resins refuse to melt on account of their hardening properties. W. Nagel has modified the Kraemer-Sarnow method, originally devised for pitches, for use with hardening resins, as follows.<sup>1</sup>

Glass tubes are used of 0.5 cm. bore, which taper conically exactly 1 cm. from the end to 0.3 cm. bore at the aperture. The sample under investigation, in the form of a very fine powder, is introduced into the tube, which is placed on a sheet of white paper, and is rammed home with a suitably shaped wooden rod. The filling of resin should reach to a mark provided on the tube 1 cm. above the aperture. As the specific gravity of the various qualities of material varies but slightly, the weight required is almost constant, namely, 0.12 to 0.15 gm. The resin particles cohere sufficiently to support the weight of 5 gm. of mercury. The charged tube, or more conveniently, two or three such tubes, as mean values must be taken, are inserted into perforated stoppers, each of which also holds a thermometer, and which serve to close wider test-tubes which act as air-baths, and which are best heated in a glycerine bath. The rate of temperature rise is of great importance. It has been found best first to heat rapidly to a temperature 25° C. lower than the softening point, as previously determined approximately, and then to remove the flame for a quarter of an hour in order to allow temperature equilibrium to be attained, after which heating is continued at such a rate that the temperature rises by exactly one degree per minute. With a little practice this is achieved without difficulty. The mercury ultimately falls through the liquifying mass in the same way as with pitches, and the temperature at which this occurs is taken as the softening point.

**Water.** The percentage of water is determined in the same manner as in cumarone resins, those products which are insoluble in xylene being tested in a finely powdered condition. Copper

<sup>1</sup> *Wiss. Veröff.* (Siemens-Konzern), IV, 321 (1925); *Farbenztg.*, 31, 1627-8 (1926).

still with inserted trays to receive the powdered sample are suitable for the purpose. Otherwise, the determination is carried out in the usual manner by Marcusson's method.<sup>1</sup>

Phenol-formaldehyde resins of the Novolak and oil-soluble types usually contain very little water. Larger proportions, of 2 per cent and over, are found in hardening resins, and still more, often over 10 per cent, in the liquid products, being largely formed during the hardening process which occurs to a considerable extent during the distillation with xylene, which involves condensation and the consequent liberation of additional water. Although the percentage of water found includes practically the whole of this chemically formed water, which is less in amount in the case of resins which harden slowly, the figures obtained furnish useful information regarding the degree to which the investigated sample had already undergone condensation, and the amount of liberated water to be anticipated during its technical application. It would be possible, by using benzene in place of the higher boiling xylene, largely to avoid the formation of water by hardening during the determination, and so to obtain a closer approximation to the amount of free water, but this would only be of interest in special cases.

**Ash.** In order to determine the ash, an accurately weighed quantity of the sample is first carefully coked over a small flame in a platinum or porcelain crucible. When nothing but coke remains this is burnt to ash in the usual manner over a strong flame on a pipeclay triangle. Any carbon which burns with difficulty is moistened with ammonium nitrate solution, dried, and re-heated.

Phenol-formaldehyde resins usually contain very small amounts of ash only. Thus, Fonrobert investigated various commercial shellac substitutes, and in no case found more than 0.6 per cent of ash; this figure may be considered as a very high limiting percentage for modern commercial products. The ash consists mainly of metallic oxides which are partially

<sup>1</sup> *Mitteilungen aus dem Materialprüfungsamt* (1904), 48; (1905), 58; Schläpfer *Angew.*, 27, 52 (1914); Liese, *Chem.-Ztg.*, 47, 438 (1923); Normann, *Angew.*, 37, 519 (1924); 38, 380 (1925).

derived from the raw materials, and partly from the material of the reaction pan. Condensing agents sometimes appear in the ash, unless they consist of ammonia or other decomposable substances. For certain applications the qualitative and quantitative investigation of the ash is necessary.

**Ammonia, and so Forth.** Ammonia and other nitrogenous bases which are used as condensing agents can easily be liberated by heating the finely divided sample with twice its weight of soda-lime after mixing well. The operation is suitably carried out in a tubulated copper retort, which is connected with a condenser and a receiver charged with standard hydrochloric acid. During the heating process air is led through the apparatus, and the air current is continued until this has cooled. The hydrochloric acid is finally titrated back with  $N/2$  - NaOH, using methyl orange as an indicator, and the quantity of base then calculated.

It should be noted that steam distillation of a solution of the resin in an aqueous caustic alkali solution does not liberate ammonia from a formaldehyde condensation product, as hexamethylene-tetramine is not decomposed by aqueous alkalies. The steam distillation method must, therefore, be considered as merely supplementary to the soda-lime method.

**Acid Ratio and Saponification Ratio.** The determination of these characteristics is carried out in the usual manner,<sup>1,2</sup> for example, with alcoholic  $N/2$  NaOH and phenol-phthalein as indicator. The following method of determining the acid ratio is stated to be particularly suitable in the case of dark resins:<sup>3</sup>

Ten grammes of the resin (Albertol) are dissolved in 100 c.c. of a neutralized mixture of 2 parts benzene and 1 part spirit; 50 c.c. of a solution of common salt are then added which has been saturated whilst hot, cooled, and then previously neutralized; 15 to 20 grm. of finely powdered common salt are also added, and, finally, 20 drops of a 1 per cent phenol-phthalein solution. The mixture is then titrated with aqueous  $N$ -NaOH solution with frequent vigorous shaking until a weak

<sup>1</sup> *Chem.-Ztg.*, 46, 513 (1922).

<sup>2</sup> Scheiber, *Lacke und ihre Rohstoffe*, Leipzig (1926), pp. 489 *et seq.*

<sup>3</sup> Communicated by Chemische Fabriken Dr. Kurt Albert, G.m.b.H.

pink coloration appears in the salt solution. A volume of neutralized spirit is then added equal to the volume of normal alkali already used for the titration, and more  $\text{N-NaOH}$  is then added until an intense crimson coloration is produced; the liquid is then titrated back with  $\text{N-H}_2\text{SO}_4$  until the intense colour changes to pale pink. This colour change is fairly sharp, and the same result is obtained on repeated back-titration.

The acid and saponification ratios of synthetic resins produced from phenols and formaldehyde only (Novolaks and hardening products) are quite small, as these products are generally of neutral or almost neutral character. Thus, for a series of shellac substitutes of Novolak type, Fonrobert<sup>1</sup> found acid ratios varying from 1.1 to 9.0. An entirely different character is shown by certain derivatives, and especially by resins soluble in benzene and in oil of the type of the Albertols, in the production of which natural resins are often used. Although these include many almost neutral products, with acid ratios below 20, other Albertol copals show acid ratios up to 150.

**Solubility.** Phenol-formaldehyde resins of the Novolak type dissolve fairly easily, and without residue, in suitable solvents, especially in spirit. If the material is to be used for polishes the behaviour on dilution must be noted, as many products fail in this respect. Oil-soluble resins must naturally be examined with regard to their solubility in, or capacity for incorporation with, those media with which they are to be used for the intended purpose (production of oil varnish).

Certain difficulties sometimes occur in testing the solubility of hardening resins. For a large number of applications these must be completely soluble in spirit; in order to test them in this respect, 1 part of the powdered sample is mixed with 2 parts of ordinary spirit in a closed bottle and allowed to stand with occasional shaking. The resin should dissolve without residue in 1 day, or at the most in 2 days, without leaving any splinter-like particles which indicate the presence of hardened resin, and with formation of a clear solution. The duration of the test may be considerably shortened by mechanical stirring or shaking or by careful heating on the water-bath.

<sup>1</sup> *Chem.-Ztg.*, 46, 513 (1922).

**Hardening Capacity.** The hardening capacity of a resin can be detected qualitatively by carefully heating a small sample. After melting has occurred, hardening quickly follows, accompanied by blister formation and frothing and followed by solidification of the hot mass.

The velocity of hardening and the character of the process are conveniently investigated by heating 5 to 10 gm. of the sample in a shallow metal dish in a drying oven at a temperature which is maintained as constant as possible, for example, at 140° C. The periods are then determined within which the molten resin thickens, or is converted into a rubber-like mass, and also the period within which it is converted into a solid whilst hot. The sample is also weighed at definite intervals, for example, every half hour, and this is continued until there is no further practical decrease in weight.

The yield of hardened resin is calculated from the total loss of weight, whilst the course of the hardening process can be deduced with sufficient exactitude from the time required for solidification. For practical purposes, special consideration must be given to the temperature at which the test is conducted, which should be in accordance with the actual working temperature used in the application of the product. The determination of the yield, which may vary within certain limits, in accordance with the temperature employed for the test, is of importance, as it not only indicates the suitability of the resin for any particular purpose, but also enables a judgment to be formed regarding its quality in general.<sup>1</sup>

The product, which has been heated till of constant weight, should be of hard and solid consistency at the temperature of the test; more particularly, it should no longer be gummy in character. The degree of transformation may be investigated by extraction of a weighed quantity with a mixture of equal parts of alcohol and acetone.

**Phenols.** The usual method of determining the so-called

<sup>1</sup> On the so-called volatility of resole resins, see von der Heyden, *Typke, Angew.*, 38, 421,521 (1925); on the other hand, see J. Scheiber, *Angew.*, 38, 904 (1925); Abonyi, *Kunstst.*, 16, 30 (1926); the latter describes the percentage yield as "rendement," and the percentage loss of weight as "hardening loss."

"free" phenols consists in distilling about 1 gm. of the powdered resin, suspended in water, in a current of steam and determining the "phenol" which appears in the distillate. The method is, however, very inexact and leads to values which are much too high, as dissociation processes occur, with liberation of further phenol. It is, therefore, better to suspend about 1 gm. of the powdered resin in benzene or toluene and distil off a portion of the hydrocarbon. The distillate is extracted with N/5 NaOH, which is then separated, acidified, and distilled in a current of steam.

According to Meighan,<sup>1</sup> the phenols are determined by dissolving the resin in a medium which is inert to metallic sodium, and measuring the quantity of hydrogen evolved by the action of sodium on the solution.

Apart from the analytical methods just described, tests are required dealing more directly with the practical application of the products, which cannot be considered in detail here on account of their extraordinary variety. Such tests, for example, on the suitability of shellac substitutes for the production of polishes, are described by Fonrobert.<sup>2</sup>

Regarding methods of testing for electrical applications, see the V.D.E. Regulations in the Appendix.

**Determination of Concentration of Resin Solutions.** Solutions of phenol-aldehyde resins are frequently used in the application of these substances, and methods of determining their concentration are of more general interest. As these resins are usually dissolved at a raised temperature there is always the possibility of evaporation of the solvent, and the quantitative proportion of the ingredients does not, therefore, necessarily enable the strength of the finished solution to be calculated, especially as the resin is frequently not completely dissolved. The determination of the resin contents of the solution offers no difficulty in those cases in which the resins undergo no change, involving loss of weight, when heated for a prolonged period. On the other hand, hardening phenol-formaldehyde resins cannot be determined by heating to

<sup>1</sup> *Ind. and Engin. Chem.*, 17, 225-237 (1925); *C.* (1925), I, 2730.

<sup>2</sup> *Chem.-Ztg.*, 46, 513 (1922).

constant weight,<sup>1</sup> as at the required temperatures of at least 100° C: further condensation takes place, varying in amount for the various products, and accompanied by loss of weight. Therefore, the drying process must be discontinued before it is completed, at a point varying with the character of the hardening resin in question. A.L. Abonyi found that certain commercial qualities of hardening resins could be successfully dried in 1½ hours at 95° C.; about 2 gm. of the resin solution were weighed in a weighing tube of 35 mm. diameter and 60 mm. in height.<sup>2</sup>

The resin contents of such solutions can, however, be determined much more rapidly and simply by means of specific gravity determinations.<sup>3</sup> As no contraction occurs when hardening phenol-formaldehyde resins are dissolved, the concentration of the solution can be calculated by means of the following equation—

$$\text{Percentage concentration} = \frac{d - d_L}{d_A - d_L} \cdot 100$$

where  $d$  is the specific gravity of the resin solution,  $d_A$  that of the solid resin, and  $d_L$  that of the solvent.

<sup>1</sup> A. L. Abonyi, *Kunstst.*, 16, 30 (1926).

<sup>2</sup> Determination of resin contents as practised in Jaroslaws Erster Glimmerwarenfabrik, Berlin.

<sup>3</sup> Abonyi, *loc. cit.*



## CHAPTER XIII

### UREA-FORMALDEHYDE CONDENSATION PRODUCTS

THE technical exploitation of urea-formaldehyde condensation products is still in its infancy,<sup>1</sup> but has attracted considerable attention through the publicity accorded to the "organic glass," Pollopas. The main aim of the development of the reaction leading to these products may be assumed to be the production of plastic masses, fast to light,<sup>2</sup> of the transparent, translucent or milky appearance of glass products, which may also be delicately tinted. The interest manifested in these products is mainly to be ascribed to their exceptional fastness to light, a quality which is extremely rare among artificial plastic masses; these new products have other excellent qualities in addition. The application of urea-formaldehyde products of resinous character, on the other hand, i.e. of products insoluble in water but soluble in organic liquids, will presumably be unimportant for the present, as the only suitable solvents for these substances which have been discovered are epichlorhydrin, dichlorhydrin, formamide, glycol ether, and so forth.<sup>3</sup> On the other hand, it may be expected that those condensation products which are soluble in water will find considerable application as adhesives, such as "Schellan." (See page 406.)

**Production.** As will be clear from the description of the reactions in the general section (page 159 *et seq.*), condensing agents play an exceptionally important part in the production of

<sup>1</sup> In this chapter the term "urea" will be used to include not only carbamide,  $\text{CO}(\text{NH}_2)_2$ , but also substituted and sulphur derivatives of all kinds, more especially thiourea.

<sup>2</sup> These products have been named "aminoplasts" in analogy to "phenoplasts" or resites; see O. Manfred and J. Obrist, *Kolloidtschr.*, 42, 175 (1927). A product analogous to Pollopas is represented by the French product "Prystal," which has been described by H. Barthélemy; see *Chim. et Ind.*, 16, 367 (1926); *Moniteur prod. chim.*, 10, No. 100, 5; *C.* (1927), II, 2630; see also the English product "Plass"; *Die Chemische Fabrik* (1928), 662.

<sup>3</sup> See British Pat. 262,818; *C.* (1927), I, 3229.

condensation products from urea and formaldehyde.<sup>1</sup> It therefore seems desirable to describe the technical methods of production under the heading of reactions without the use of condensing agents, and those carried out in the presence of acid and alkaline condensing agents respectively, after which other processes will be considered.

**Condensations in the Absence of Condensing Agents.** N. John must be recognized as the first to realize the technical utility of urea-formaldehyde products. In his patent specifications he confines himself to condensation in the absence of condensing agents.<sup>2</sup> The reaction is effected by prolonged heating<sup>3</sup> of 1 part of urea with 5 to 6 parts of 40 per cent formaldehyde solution.<sup>4</sup> After distilling off the water, various products are obtained according to the time of heating, namely, either gum-like aqueous solutions of water-soluble substances, capable of being used as adhesives, or by more prolonged heating, products which gelatinize in the cold and which may be converted into solid masses, insoluble in water and in alcohol, by heating to 80° C. (hardening process). According to F. Pollak and K. Ripper, however, the gum-like products smell strongly of formaldehyde, and coagulate after a few days, with loss of solubility.<sup>5</sup> Moreover, the hardened masses have usually a blistered, swollen, and foam-like structure.

In these and other processes ordinary urea may be replaced by thiourea or other urea derivatives, such as acetylthiourea. The products are intended for use as adhesives, varnishes, or impregnating agents, or as substitutes for rubber, ebonite, celluloid or horn, according to their respective properties. It should also be pointed out that the formaldehyde solutions

<sup>1</sup> H. Scheibler, F. Trostler, E. Scholz, *Angew.*, 41, 1305 (1928).

<sup>2</sup> Austrian Pat. 78,251 (1918); *Kunstst.*, 10, 119 (1920); German Pat. 392,183 (1918); *C.* (1924), II, 1283; U.S. Pat. 1,355,834 (1920); *Kunstst.*, 11, 78 (1921); British Pat. 151,016 (1920); *C.* (1921), II, 192; Swiss Pat. 94,687 (1922); *C.* (1923), II, 1042; Dutch Pat. 9,542; *C.* (1923), IV, 893.

<sup>3</sup> On condensation at the ordinary temperature, see von Girssewald, Siegens, *Ber.*, 47, 2465 (1914).

<sup>4</sup> Polymerized formaldehyde products are used by D. Beck, Swiss Pat. 92,984; see also H. Traun & Söhne, French Pat. 618,991; British Pat. 271,264; *C.* (1928), I, 1584; see also U.S. Pat. 1,658,359; see also Rohm & Haas Co., F. Lauter, U.S. Pat. 1,633,337; French Pat. 619,342; *C.* (1928), I, 1335, etc.

<sup>5</sup> *Chem.-Ztg.*, 48, 569 (1924).

used by John contain formic acid in their usual commercial form, so that the reaction actually takes place in an acid, and not in a neutral medium.<sup>1</sup>

Urea reacts much more rapidly than thiourea, and this renders the uniform dehydration of the product more difficult. With thiourea one may evaporate without special precautions, and even blow in hot air or hot inert gases, without any fear of faulty results. The same process may also be applied to suitable mixtures of thiourea and urea.<sup>2</sup>

**Condensations with Acid Condensing Agents.** H. Goldschmidt and O. Neuss<sup>3</sup> use at least 3 per cent of acid,<sup>4</sup> calculated on the weight of urea, as a condensing agent. One hundred parts of urea are dissolved in a dilute formaldehyde solution, which contains not more than 120 parts of formaldehyde; the liquid is then heated until frothing occurs, and the acid added. Turbid, porous masses are obtained, resembling meerschäum.

In further patents<sup>5</sup> the same inventors describe condensation by heating in presence of water and small amounts of acids or of salts of non-alkaline reaction. Perfectly transparent rapidly hardening masses are thus obtained, and 15 to 17 per cent less formaldehyde is used than is the case in the absence of condensing agents. It is also stated to be advantageous for some purposes, and especially in order to obtain products more resistant to water, or suitable for varnish production, to use acid

<sup>1</sup> On reactions in a neutral medium, see German Pat. 416,252 (1923); *C.* (1923), II, 2101; on the action of radiations of short wave length; also French Pat. 609,108 (1926); Swiss Pat. 114,289 (1925); *C.* (1926), II, 2502; on condensation under increased pressure; see also Swiss Pat. 104,339; *C.* (1924), II, 1282. According to Rohm & Haas Co., F. Lauter, U.S. Pat. 1,671,598; *C.* (1928), II, 1392, the hot urea solution is gradually introduced into a boiling formaldehyde solution. In a later patent (U.S. Pat. 1,672,848; *C.* (1928), II, 1828) the further addition of aromatic sulphonamides is recommended; after-treatment, for example, with oxalic acid, is also claimed.

<sup>2</sup> British Cyanides Co., Ltd., E. Ch. Rossiter, British Pat. 248,477; 266,023; French Pat. 623,983; *C.* (1928), I, 1336.

<sup>3</sup> German Pat. 412,614 (1921); *C.* (1925), II, 356; *Kunstst.*, 15, 124 (1925); British Pat. 187,605 (1922); *C.* (1923), IV, 951; *Kunstst.*, 13, 125 (1923); 14, 41 (1924); Austrian Pat. 102,791 (1922); *C.* (1926), II, 114.

<sup>4</sup> For example, sulphuric acid; in other patents, oxalic acid, tartaric acid, citric acid, bisulphate, acid oxalates, the hydrochlorides of aromatic bases and other substances are mentioned; see British Pat. 258,950 of British Cyanides Co., Ltd., and E. C. Rossiter; *C.* (1927), I, 820.

<sup>5</sup> Austrian Pat. 95,663 (1922); Swiss Pat. 103,221; British Pat. 208,761; French Pat. 556,529 (1922); *C.* (1924), II, 2420; *Kunstst.*, 15, 12 (1925).

condensing agents of such a character that they themselves react with formaldehyde with formation of plastic masses; phenols and casein are examples of such acid condensing agents.

According to F. Pollak and K. Ripper,<sup>1</sup> the transparent products obtained by these processes contain bubbles, whilst the turbid products are full of cracks, and the meerschäum substitutes are unstable and fall into small pieces in a few days. In fact, the extremely rapid hardening which occurs in the presence of acid condensing agents and the accompanying liberation of water and formaldehyde appears to render the production of satisfactory plastic masses difficult. This is indicated by the patent dealing with the application of these products, according to which they are to be ground and then compressed at temperatures of 100° C. and over.<sup>2</sup>

A method of producing transparent products has been patented<sup>3</sup> which differs from that of Goldschmidt and Neuss, by the use of at least 2.4 mol. of formaldehyde per molecule of urea, in the presence of mineral acids at raised temperatures. In order to remove the water produced by the condensation, it was found to be advantageous to add organic solvents during the production of the product, such as glycol chlorhydrin, glycol monoacetate, formamide, formic acid, glacial acetic acid, or mixtures of these, and to distil. Clear, colourless solutions are first obtained, which if used directly as varnishes yield colourless, perfectly transparent coatings. A further improvement was achieved<sup>4,5</sup> by replacing the remaining quantities of volatile solvent in the products obtained as just described, by non-volatile or high-boiling organic substances which are capable of forming solid solutions with the condensation

<sup>1</sup> *Chem.-Ztg.*, 48, 569 (1924).

<sup>2</sup> Chemische Fabrik Ambra, Akt.-Ges. (assigned by H. Goldschmidt and O. Neuss), British Pat. 202,651 (1923); *C.* (1925), I, 1455; Austrian Pat. 101,453; *C.* (1926), I, 2623; Dutch Pat. 15,567; *C.* (1927), I, 3229; Faucher, French Pat. 569,823 (1923); *C.* (1925), I, 2262.

<sup>3</sup> Badische Anilin- und Soda-Fabrik, German Pat. 409,847 (1922); *C.* (1925), I, 1910; *Kunstst.*, 15, 182 (1925).

<sup>4</sup> Badische Anilin- und Soda-Fabrik, German Pat. 403,645 (1922); *C.* (1925), I, 309, *Kunstst.*, 15, 84 (1923).

<sup>5</sup> German Pat. 404,024 (1922); Badische Anilin- und Soda-Fabrik, *C.* (1925), I, 908; *Kunstst.*, 15, 123 (1925); see also I. G. Farbenind., A.-G., British Pat. 262,818; *C.* (1927), I, 3229.

product. For example, cellulose esters, natural or synthetic resins, or plasticizers, such as camphor or camphor substitutes, are added to the solutions. The liquid or solid solutions or homogeneous mixtures so obtained are intended for use in the production of varnishes, adhesives, artificial silk, films, plastic masses, and so forth.

According to recent processes of the Gesellschaft für Chemische Industrie, Basle,<sup>1</sup> hard resistant products, free from bubbles or cracks, are stated to be obtained with considerable economy of formaldehyde as follows: 1 molecular proportion of urea and at least 2 molecular proportions of formaldehyde are converted into a primary condensation product under neutral conditions by heating for 3 to 4 hours under pressure, or for 30 hours under reflux. The primary product so obtained is dehydrated in a special manner. By making use of the observation that the addition of urea greatly reduces the viscosity of solutions of the primary product, it is easily arranged by suitable regulation of the quantity of urea, which must not be less than 1.05 mol. per 2 mol. of formaldehyde, that the required dehydration shall not be vitiated by premature large increase of the viscosity. Acid substances, such as ammonium chloride, ammonium sulphate, sulphuric acid and phosphoric acid are used as catalysts. The products are either perfectly transparent or more or less cloudy (translucent like alabaster). According to another patent of the same firm,<sup>2</sup> the interaction between the components is at first caused to take place in the presence of active charcoal, which can be removed at any phase deemed desirable. The reaction may be effected either in the heat or in the cold. Moreover, organic substances, such as alcohols, ketones, ethers, esters or mixtures of these, may be used to retard the reaction, a measure which offers advantages, especially in the presence of acid condensing agents.

Gaseous substances of acid character, which may if desired be used in solution, are especially suitable for hardening the viscous products previously obtained under neutral conditions.

<sup>1</sup> British Pat. 249,101; French Pat. 611,271; Swiss Pat. 117,170; *C.* (1927), II, 982.

<sup>2</sup> French Pat. 616,495; Swiss Pat. 118,725; *C.* (1927), II, 983; see also U.S. Pat. 1,676,543.

Such substances are sulphur dioxide, formic acid, hydrofluoric acid, hydrochloric acid, and so forth.<sup>1</sup>

According to H. John,<sup>2</sup> urea or its derivatives, which are costly, may be replaced as raw materials for the manufacture of plastic masses by calcium cyanamide, which is cheap and readily obtainable. Commercial calcium cyanamide is extracted with warm water and the solution, which contains calcium cyanamide, dicyanamide, urea, calcium carbamate and guanidine, is treated with acid if required, and then condensed with formaldehyde in presence of acid. Another interesting patent describes the utilization of a mixture of carbon monoxide and ammonia under pressure, in presence of suitable catalysts.<sup>3</sup> Regarding the production of condensation products from urea, and so forth, with acrolein, the reader is referred to the patents of the Gesellschaft für Chemische Industrie, Basle.<sup>4</sup>

**Condensing with Basic Condensation Agents.** Basic condensing agents proved very advantageous for the reaction between urea and formaldehyde, more particularly on account of the resulting economy of formaldehyde; this is probably mainly due to the property of condensing agents of this class of accelerating the production of an intermediate product, which is probably a methylolurea, without influencing the further liberation of water, which is greatly accelerated by acid agents.

F. Pollak<sup>5</sup> effected the condensation of urea (1 mol.) with formaldehyde (up to 3 mol., but preferably 2 mol. only) in the

<sup>1</sup> I. G. Farbenindustrie A.-G., British Pat. 259,950; *C.* (1928), I, 2464; 264,466; *C.* (1928), II, 1499; see also Swiss Pat. 125,011; see also Société Industrielle des Matières Plastiques, French Pat. 615,346; *C.* (1928), I, 1335; acid anhydrides, such as benzoic and acetic anhydrides, alcohols, sodium phosphate, sodium acetate, sodium glycolate, etc.; see also F. Pollak, K. Ripper, British Pat. 240,840, 266,389; French Pat. 603,875; Austrian Pat. 107,427; *C.* (1928), I, 264.

<sup>2</sup> German Pat. 394,488 (1919); *C.* (1924), II, 1136; *Kunstst.*, 15, 122 (1925); on the condensation of dicyandiamide with formaldehyde, see also H. Wallach, German Pat. 323,655, 325,647; K. Ripper, British Pat. 287,177; *C.* (1928), II, 293; the utilization of cyanamide is described by American Cyanamid Co., U.S. Pat. 1,658,597; *C.* (1928), I, 1809.

<sup>3</sup> H. Spindler, French Pat. 637,051; *C.* (1928), II, 190.

<sup>4</sup> British Pat. 260,288; French Pat. 623,037; *C.* (1927), II, 983; see also U.S. Pat. 1,654,215.

<sup>5</sup> British Pat. 171,094 (1921); French Pat. 542,971; *C.* (1922), II, 749; German Pat. 418,055 (1921); *C.* (1925), II, 2103; see Soc. Industrielle des Matières Plastiques, H. Barthélemy, U.S. Pat. 1,645,848; *C.* (1928), I, 1335; alkaline earth carbonates.

presence of bases such as ammonia, hexamethylene tetramine, pyridine, or urea itself. The primary product which was obtained was a colourless liquid, soluble in water,<sup>1</sup> which could be converted into a hard, infusible, transparent product, insoluble in acids and alkalis, by concentration in vacuo to a syrup, filling this into moulds and the subsequent action of heat, at 60–80° C., or of combined heat and pressure. The direct conversion of the gummy solution of the primary condensation product, which had but little odour of ammonia, even with careful heating, resulted in the formation of transparent solid masses, of slightly yellowish colour, in the case of small quantities only. Larger masses always showed cracks and other discontinuities.<sup>2</sup>

The reactions which accompany these changes were closely studied by F. Pollak and K. Ripper, who included an investigation of their colloid-chemical character; their investigations were based on Ripper's observation,<sup>3</sup> that the presence of salts influenced the character of the primary condensation products in manners varying greatly with the nature of the salt in question. Thus the gelatinization of the solutions of the primary products is retarded by the addition of salts of alkaline reaction, and especially by the alkali salts of weak inorganic and organic acids, such as sodium acetate. This stabilization can be effected at any degree of viscosity, and by concentration at low temperatures in vacuo, non-gelatinizing solutions of 90 per cent concentration can be obtained. On the other hand, neutral salts of strong acids with strong bases caused acceleration of the gelatinizing process and spontaneous syneresis (separation of water from the gel). However, six to nine months are required to produce even small quantities of perfect solid fragments of the hard colloid by such syneresis in the cold. Acid salts, especially ammonium salts, cause almost immediate gelatinization of the intermediate product, with formation of a white product, containing water in a coarsely dispersed condition.

<sup>1</sup> On its application, see F. Pollak, British Pat. 157,416 (1921).

<sup>2</sup> F. Pollak, K. Ripper, *Chem. Ztg.*, 48, 569, 582 (1924).

<sup>3</sup> British Pat. 181,014 (1921); *C.* (1923), IV, 950; *Kunstst.*, 13, 125 (1923); Swiss Pat. 104,801 (1922); Canadian Pat. 232,635 (1922); *C.* (1924), I, 1716; see also British Pat. 213,567 (1923).

By combining these various effects with the hardening caused by temperature rise, which is accompanied by the liberation of formaldehyde and consequent formation of cracks, it was found that the hydrogen ion concentration during the final stages of the distillation should be so adjusted that syneresis can still take place, but that the liberation of formaldehyde, which is promoted by the presence of acids, can be avoided. Thus, at a hydrogen ion concentration of  $10^{-4}$  to  $10^{-7}$  at  $100^{\circ}\text{C}$ ., hardened products free from cracks can be obtained. When masses were hardened at hydrogen ion concentrations approaching  $10^{-7}$  cloudiness occurred, which could be avoided by the addition of neutral salts. These proved to be effective in the order of Hofmeister's ionic series; thus the clearing effect of potassium chloride is but slight, whereas sodium and calcium chlorides are completely effective. Whilst sulphates exercise scarcely any clearing effect, and chlorides are very effective, the heat effects are produced with salicylates.<sup>1</sup>

The results of these investigations were embodied in various patent specifications. Thus, the recommendation is made to remove by suitable means the excess of formaldehyde present in the initial condensation product, which proves to be very objectionable during subsequent hardening, owing to formation of cracks, and so forth;<sup>2</sup> the precautions recommended comprise the addition of substances which react with formaldehyde, such as urea, phenol, and so forth, or treatment with reagents which destroy formaldehyde, such as hydrogen peroxide. Hardening may then take place safely at temperatures of  $90^{\circ}\text{C}$ . and over, at which the highest degree of polymerization is attainable. The products so obtained are distinguished from other formaldehyde-urea products by yielding an odourless dust. The acid reaction which is produced even if primary condensation products obtained in the presence of basic condensing agents, is counteracted by the addition of

<sup>1</sup> F. Pollak, French Pat. 568,985 (1923); *C.* (1924), II, 1283.

<sup>2</sup> F. Pollak, Swiss Pat. 104,339 (1923); French Pat. 562,320 (1923); *C.* (1924), II, 1282; F. Pollak, K. Ripper, U.S. Pat. 1,507,624 (1923); *C.* (1925), I, 1455; F. Pollak, German Pat. 437,533 (1922); French Pat. 611,973; Austrian Pat. 103,910; *C.* (1927), I, 1754; Australian Pat. 999 (1926).



bases or basic salts.<sup>1</sup> A clarifying material is also added, such as sodium chloride.

One may proceed, for example, as follows—

Urea is heated with formaldehyde and hexamethylene tetramine until a clear, homogeneous liquid is formed; sodium acetate is then added to prevent the product from gelatinizing too rapidly, and the greater portion of the water is evaporated in vacuo; the acidity of the liquid is then determined by titration, and sufficient urea is added both to combine with the excess of formaldehyde and to neutralize the acid reaction. Water is then distilled off until the product can be poured, and sodium chloride is added, either during the distillation or immediately afterwards. The product is finally cast in moulds and hardened at 60–100° C. A perfectly transparent product is so obtained.

Finally, the production of the viscous primary condensation product may be effected in two stages under the influence of different condensing agents;<sup>2</sup> the first stage consists in boiling a neutral or basic mixture of urea and formaldehyde for a short period, whilst the second stage is carried out in the presence of hydrogen ions (acids). The action of acid is thus transferred to a comparatively early stage of the production processes, and the primary product is thus obtained in a form more or less insoluble in water.

In order to obtain strongly hydrophobic primary products, which are highly viscous (and can consequently retain almost unlimited proportions of fillers) and which form exceptionally insensitive final products,<sup>3</sup> of excellent insulating properties, the mixture of the components is first heated for a considerable time, after which substances suitable for the removal of the excess of formaldehyde are added, such as thiourea or phenols, and the reaction mixture is further heated in the presence of hydrogen ions until the hydrophobic resinous product

<sup>1</sup> F. Pollak, French Pat. 568,985 (1923); *C.* (1924), II, 1283.

<sup>2</sup> F. Pollak, Austrian Pat. 99,415 (1923); French Pat. 581,488 (1924); *C.* (1925), II, 785; *Kunstst.*, 16, 57 (1926); see also German Pat. 456,082.

<sup>3</sup> F. Pollak, Austrian Pat. 103,910; French Pat. 611,973; *C.* (1927), I, 1754; see also K. Ripper, British Pat. 287,177; *C.* (1928), II, 293; 287,568; *C.* (1928), II, 1155.

is precipitated on cooling. Apart from substances which supply H-ions, other polymerizing substances, which do not liberate OH-ions, may be added. The mixture may be neutralized or rendered slightly alkaline before cooling. Even in this case the hardening of large masses is attended with difficulties, which were overcome by the use of moulds which are permeable by the dispersing agent, but impermeable by the colloid.<sup>1</sup>

It has been found possible to overcome the various disadvantages presented by the gels obtained from aqueous solutions, by adding substances, at suitable stages of the reaction, which possess the property of displacing the water in the gels. Various organic solvents have been found suitable for this purpose, for example, hydrocarbons, alcohols, esters, aldehydes, ketones, acids, and so forth. A special advantage arises from the fact that cellulose esters, resins, camphor, casein, phenols, and so forth, may also be present, thus leading to products of the most various applications.<sup>2</sup>

A few other processes must be referred to, which resemble in principle those already described. Thus, plastic masses are obtained<sup>3</sup> if dimethylolurea or mixtures of di- and monomethylol urea, i.e. of substances which are obtainable by the alkaline condensation of formaldehyde with urea, are heated to comparatively high temperatures with various additions, with or without the application of pressure; hardening or hardened products may be obtained by acidifying a condensation product obtained from urea with formaldehyde in the presence of alkali.<sup>4</sup>

**Various other Processes.** Attempts have been made to

<sup>1</sup> F. Pollak, K. Ripper, *Chem.-Ztg.* 48, 569, 582, (1924).

<sup>2</sup> F. Pollak, K. Ripper, *British Pat.* 238,904; *French Pat.* 602,318; *Austrian Pat.* 107,429; *C.* (1928), I, 265; I. G. Farbenindustrie A.-G., *British Pat.* 261,029; *C.* (1928), II, 1828; F. Schmidt, *British Pat.* 281,993; *C.* (1928), I, 2213; *Gesellschaft für chemische Industrie in Basel*, *British Pat.* 281,717; *C.* (1928), I, 2213; on the production of a resinous product from urea, phenol, and formaldehyde, see *Damard Lacquer Co., Ltd.*, W. F. Fleet, H. V. Potter, *British Pat.* 256,711; *C.* (1928), I, 2465.

<sup>3</sup> C. Ellis, *U.S. Pat.* 1,536,881 (1922); *C.* (1925), II, 784; *Kunstst.*, 15, 221 (1925).

<sup>4</sup> C. Ellis, *U.S. Pat.* 1,536,882 (1922); *C.* (1925), II, 785; *Kunstst.*, 15, 221 (1925); *U.S. Pat.* 1,482,357-8 (1922); *C.* (1924), II, 1744; *Kunstst.*, 15, 163 (1925).

influence the condensation of urea with formaldehyde by means other than condensing agents. Thus, the use for the purpose of rays of short wave length<sup>1</sup> or of condensation under high pressure<sup>2</sup> have been proposed. A process may also be referred to, according to which urea is first condensed with carbohydrates in presence of acid catalysts, after which the product is heated with formaldehyde, and so forth, with or without the application of pressure.<sup>3</sup> According to the duration of the hardening process, either soluble resins or insoluble, infusible plastic masses are obtained.

In place of formaldehyde (and apart from acrolein), the use of alcohols or ketones has been proposed as reacting components, in the presence of suitable amino-derivatives, not belonging to the urea group, such as aromatic acid amides; the addition of a reducing agent, such as zinc dust, sodium amalgam, magnesium powder, and so forth, is also necessary.<sup>4</sup>

### PROPERTIES AND APPLICATIONS OF UREA-FORMALDEHYDE PRODUCTS

Among urea-formaldehyde condensation products, the best known commercially are those marketed as "Schellán" and "Pollopas,"<sup>5</sup> and a description of the properties and applications of such products may therefore be based on those sold under the above names. Other similar products, some of which have been more closely described in the preceding pages, more or less resemble the above-mentioned commercial qualities.

Schellán is the aqueous solution of the primary condensation

<sup>1</sup> Badische Anilin- und Soda-Fabrik, German Pat. 416,252 (1923); *C.* (1925), II, 2101; *Kunstst.*, 16, 56 (1926); Austrian Pat. 101,656 (1924); French Pat. 605,970 (1925); *C.* (1926), II, 1791; German Pat. 437,646 (1924); *C.* (1927), I, 528; ultra-violet light also accelerates the hardening process and prevents the development of opacity, and so forth.

<sup>2</sup> Gesellschaft für chemische Industrie, Basel, French Pat. 609,108 (1926); Swiss Pat. 114,289 (1925); *C.* (1926), II, 2502; see also U.S. Pat. 1,674,199, 1,679,246.

<sup>3</sup> J. S. Stokes, British Pat. 209,697 (1922); *C.* (1926), II, 1473; *Kunstst.*, 16, 254 (1926).

<sup>4</sup> I. G. Farbenindustrie A.-G., British Pat. 287,095; *C.* (1928), II, 190; 290,192; *C.* (1928), II, 2071.

<sup>5</sup> Kunstharzfabrik Dr. Fritz Pollak, G.m.b.H., Vienna; this firm very kindly placed various information at our disposal.

product obtained by Pollak's patented process. The colourless perfectly transparent, gum-like solutions are supplied in various concentrations and of various degrees of viscosity. They show the typical properties of sols of highly solvated, hydrophilic colloids. They may be preserved indefinitely, without gelatinizing, by the addition of salts of basic tendency, such as sodium acetate. Such solutions are widely used as colourless water-varnishes, adhesives, binding agents, impregnating agents and stiffening agents.<sup>1</sup>

Varnishes are also obtained by mixing the condensation products with non-volatile substances of such a character that they form solid solutions with the urea derivative.<sup>2</sup>

Pollopas is the insoluble and infusible end-product obtained by Pollak, which carbonizes at temperatures above about 300° C. It forms a perfectly clear, transparent and colourless mass, completely fast to light, which is highly lustrous and takes a high polish. These properties justify its description as "organic glass." The wide applicability of the product is clear from the following account of its properties: specific gravity, 1.44 (i.e. one-half of that of glass); hardness, 2.95 on the Mohs scale; it transmits the ultra-violet rays of sunlight as far as about 270 $\mu$ ; index of refraction, 1.54 to 1.9; low dispersion; resistance to compression, 2,230 kg. per sq. cm.; tensile strength 10 kg. per sq. cm.; transverse strength, 510 kg. per sq. cm.; thermal conductivity, 0.00184 C.G.S. units; it is not attacked in the cold by either aqueous or alcoholic solutions, and only slightly when hot; the absorption of cold water in 24 hours is 0.1 to 0.2 per cent.<sup>3 4</sup>

Pollopas is about as hard as copper, and differs from glass

<sup>1</sup> See F. Pollak, German Pat. 405,516 (1919); British Pat. 157,416 (1921); on an application for the production of ornamental effects on textiles, leather, and the like, see J. C. Vredenburg, French Pat. 593,442 (1925); *C.* (1926), I, 1349.

<sup>2</sup> I. G. Farbenindustrie A.-G., Swiss Pat. 125,725; *C.* (1928), II, 2292; French Pat. 641,420; *C.* (1928), II, 2071; F. Pollak, K. Ripper, British Pat. 238,904; French Pat. 602,318; Austrian Pat. 107,429; *C.* (1928), I, 265.

<sup>3</sup> O. Manfre and J. Obrist, *Kolloidzechr.*, 42, 177 (1927), found for Pollopas a maximum transverse strength of 600–850 kg. per sq. cm. and a modulus of elasticity of 31,000–38,000 kg. per sq. cm.; compare the corresponding values for phenoplasts, p. 338.

<sup>4</sup> On the behaviour under chemical influences, see H. Scheibler, F. Trostler, and E. Scholz, *Angew.*, 41, 1305 (1928).

by the fact that it can be turned on a lathe, and can also be bored, ground, filed, carved, and polished. As it has a low specific gravity and can easily be coloured or clouded in the mass, it can be used for the production of ornaments and smoking utensils, imitation gems and pearls, buttons, billiard balls, handles, and so forth. Its excellent optical properties enable it to be advantageously used instead of flint glass and also for prisms and lenses. As urea-formaldehyde condensation products absorb ultra-violet rays but slightly, they can be used for optical instruments in place of quartz glass.<sup>1</sup>

By carrying out the gelatinization and hardening processes accordingly, one can obtain white, opaque, porcelain-like masses or products resembling meerschaum, the turbidity of which is due to finely dispersed water.<sup>2</sup>

The various products are converted into shaped articles by casting or pressure moulding. In order to obtain satisfactory results the products to be worked must be in an exactly suitable condition, as otherwise the resulting articles may not be durable. Further details will be found in the patent specifications dealing with the production and working of unfilled and filled plastic masses. The essential requirement is that the condensation shall be carried to a certain definite stage at which the material is sufficiently dehydrated, but is still fusible or capable of gelatinizing with certain solvents. It can then be formed and finally hardened by heat and pressure,<sup>3</sup> or in other ways.<sup>4</sup> In the case of filled products similar precautions are necessary, especially if the fillers are entirely inorganic. Products filled with gel-producers of the character referred to previously (pages 400, 404) are more easily worked, and are especially suitable for pressure moulding. Those products which are clear are called "Pollopas," "Fantasite H," and so forth; opaque moulded products are known as "Trolite Special E," "Bandalasta," and so forth. Objects of very varied character

<sup>1</sup> Badische Anilin- und Sodafabrik, German Pat. 416,753 (1923); *C.* (1926), I, 250; see C. Plonait, *Glastechn. Ber.*, 5, 354 (1927); *C.* (1928), I, 120, on the results obtained with various varieties of Pollopas.

<sup>2</sup> Dr. Fritz Pollak, Ges. m.b.H., British Pat. 261,409; French Pat. 624,441; *C.* (1928), II, 1499.

<sup>3</sup> F. Pollak, K. Ripper, Austrian Pat. 109,532; *C.* (1928), II, 1499.

<sup>4</sup> See Footnote (1), p. 401.

are produced, such as ornaments, fancy goods, smoking utensils, buttons, handles, boxes, covers, combs, and so forth. In consequence of the very considerable elasticity of some of these products they are also used for the production of fibres, such as horse-hair substitutes, and for films, plates, tubes, and so forth. The possibility of removing the greater part of the water enables them to be also used for all kinds of articles for the electrical industry.

The use of these products has also been proposed for purposes for which other hardening products, such as resoles, are already utilized. Thus it has been suggested that their solutions should be applied to materials which could then be wound and hardened to produce various products. Fibrous or porous materials, such as wood, can also be impregnated and converted into valuable products by subsequent hardening. As the material does not swell in organic liquids it can be used advantageously for the production of special tubing.<sup>1</sup>

Processes have also been devised for reconverting insoluble urea-formaldehyde condensation products into the soluble form.<sup>2</sup> This is stated to be effected, for example, by heating with an excess of formaldehyde to temperatures of over 110° C., which is conveniently done under pressure. When reconverting into the soluble form products which have been hardened with considerable amounts of hydrochloric acid, it is advisable to neutralize the formaldehyde used for the purpose by the addition of bases. By these means the waste obtained during mechanical working, such as sawdust and shavings, can be quantitatively recovered and re-utilized, as the solutions can be converted into ordinary primary condensation products after adding urea. The same purpose may be effected in another manner by conversion of the waste into colloidal sols, for which several methods are known.<sup>3</sup>

<sup>1</sup> V. Lefebure, British Pat. 258,968; *C.* (1927), I, 820.

<sup>2</sup> Gesellschaft für Chemische Industrie, Basle, French Pat. 609,109 (1926); Swiss Pat. 114,705 (1925); *C.* (1926), II, 2502.

<sup>3</sup> F. Pollak, K. Ripper, British Pat. 240,840, 266,389; French Pat. 603,875; Austrian Pat. 107,427; *C.* (1928), I, 264.



# APPENDIX

Regulations of the V.D.E. (Association of German Electrical Engineers) for the examination of electrical insulating materials.<sup>1</sup>

Valid as from 1st October, 1924.<sup>2</sup>

## V.D.E. 318<sup>3</sup>

**Introductory.** The investigation of electrical insulating materials includes the following determinations—

### MECHANICAL AND THERMAL TESTS.

1. Bending strength.
2. Impact-bending strength.
3. Ball-hardness.
4. Heat resistance.
5. Fire resistance.

### ELECTRICAL TESTS.

1. Surface resistance.
2. Internal resistance.
3. Arc resistance.

## SHAPE OF SAMPLES

The normal samples to be used for the tests are flat bars, the dimensions of which are as follows—

Thickness	.	.	.	$a = 10$ mm.
Breadth	.	.	.	$b = 15$ mm.
Total length	.	.	.	$L = 120$ mm.

<sup>1</sup> These regulations, which are of exceptional interest to the synthetic resin industry, have been reproduced here by the kind permission of the "Verband Deutscher Elektrotechniker, E.V." (Association of German Electrical Engineers).

<sup>2</sup> *Elektrotechn. Zeitschr. (E.T.Z.)*, (1922), 445; (1923), 557, 768; (1924), 934; the acceptance of these regulations followed at the Annual Meeting of the V.D.E. in 1924.

<sup>3</sup> We have reproduced the additions published as V.D.E. 318a, in July, 1927 (*E.T.Z.* (1927), 156, 860), which were accepted as from 1st July, 1927. A revised edition of V.D.E. 318 has just appeared, and we have followed any purely objective small alterations which it contains, but it was no longer possible to reproduce exactly any slight verbal alterations.



The total number of samples required for an investigation is: for (a) *Mechanical and Thermal Tests*, at least 30 normal bars; for (b) *Electrical Tests*, 12 normal bars.

## METHODS OF TESTING

### Mechanical and Thermal Tests

#### *Bending Strength.*

(a) Five tests with the material as supplied.

( $\beta$ ) Five tests after storage for 30 days in petroleum at room temperature.

The test is to be carried out at room temperature, as shown in Fig. 14.<sup>1</sup> The force  $P$  is applied half-way between the sup-

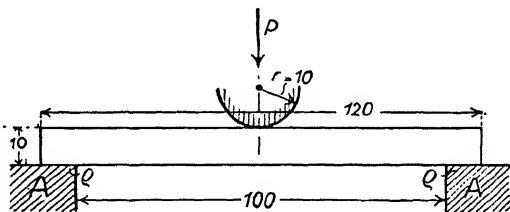


FIG. 14

ports  $A A$ , by a pressure beam, the radius of curvature  $r$  of which is 10 mm. The pressure beam must be so disposed that it makes line contact with the sample without constraint. The edges of the supports are to be rounded at  $Q$ , with a radius of curvature  $r$  of 1 mm. The distance between supports is to be 100 mm.

Care must be taken that the load is applied without shock, and that it is reliably measured. Care must also be taken that the sample lies evenly on the supports  $A A$ .

The load is to be increased at a uniform rate of 250 kg. per sq. cm. per minute, until breakage occurs.

The total amount of bending may be determined with sufficient accuracy on a millimetre scale.

<sup>1</sup> The figures are numbered consecutively with those in the earlier part of this book, and not as in the original.

*Impact Bending Test.*

( $\alpha$ ) Five tests at room temperature.

( $\beta$ ) Five tests at about  $-20^{\circ}\text{C}$ .

(Tests  $\beta$  are only required for materials which are to be used in the open.)

The tests are to be carried out with a standard pendulum impact machine.

The impact beam is to have an edge of  $45^{\circ}$  angle, which is to be rounded off at the apex, with a radius of curvature of 3 mm.

The distance between supports is 70 mm.

The supports must be disposed as in Fig. 15, recessed at an angle of  $15^{\circ}$ , and the supporting edges are to be rounded off at Q with a radius of curvature of 3 mm., in order that the samples may pass through the supports without hindrance.

The results are to be expressed in centimetre-kilograms per square centimetre.

*Ball Hardness.*

Five tests at room temperature. ( $15-25^{\circ}\text{C}$ .)

A steel ball of 5 mm. diameter ( $R = 0.5\text{ cm.}$ ) is pressed on to the sample, without impact, at a constant pressure of 50 kg. The depth of the impression is measured after 10 and 60 sec. From these the degree of hardness  $M$  (in kg. per sq. cm.) is calculated according to the formula:

$$H = \frac{P}{\pi \cdot n \cdot D} - \frac{C}{h}$$

The impressions must be made in the centre of the samples, which are 15 mm. in width.

**Heat Resistance<sup>1</sup>**

*With the Martens Apparatus.* (Three Tests)

The samples, which are firmly held in a position vertical to

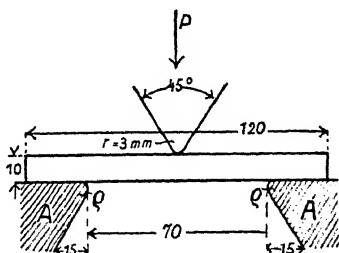


FIG. 15

<sup>1</sup> From V.D.E. 318a.

the base-plate *g* (Fig. 16), are subjected to a constant bending load of 50 kg. per sq. cm. by the attached weighed lever *h*, and are slowly heated. The rate of temperature rise shall be

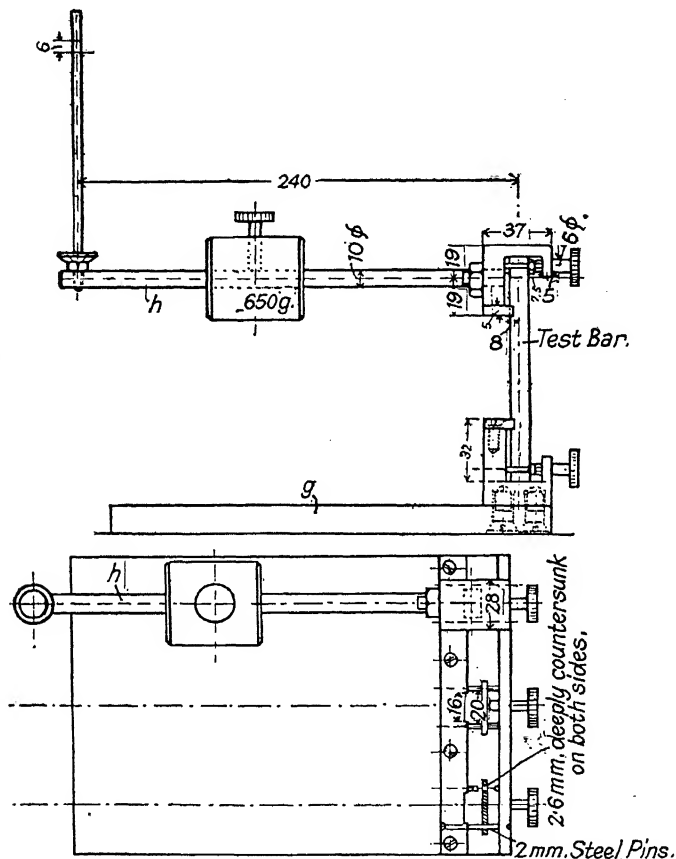


FIG. 16

50° C. per hour. The Martens degree  $A_M$  is determined, i.e. the temperature at which the lever *h* falls through 6 mm. at a distance of 240 mm., or at which the sample breaks.

*With the Vicat Needle. (Three Tests)*

A cylindrical steel needle with a flat-ground end of 1 sq. mm.

cross-section (1.13 mm. diameter) is permanently loaded with a weight  $G$  of 5 kg. and placed vertically on the normal sample bar, which lies in a horizontal position. (See Fig. 17.) The depth of penetration of the needle is observed with at least 10-fold magnification, relatively to the light contact member  $S$ . The temperature is to be increased as for previous test. The Vicat degree  $A_v$  is determined, i.e. the temperature at which the needle has penetrated the sample to a depth of 1 mm.

#### *Fire Resistance. (Three Tests)*

A normal sample bar is clamped in a horizontal position, and exposed for 1 min. to the flame of a Bunsen burner fed with lighting-gas. The burner aperture shall be of 9 mm. diameter, and the height of the flame when the burner is placed vertically shall be 10 cm. The burner is to be inclined at an angle of  $45^\circ$ , and the bar is to be introduced into the flame in such a position that the lower surface of the bar, which is 15 mm. wide, shall be 3 cm. above the upper edge of the burner, and that its end surface shall be at a horizontally measured distance of 1 cm. from the lower rim of the burner. (See Fig. 18.)

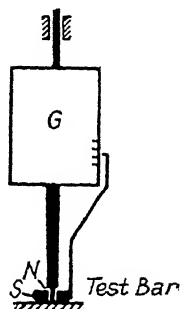


FIG. 17

The behaviour of the insulating material is to be recorded relatively to the following three degrees of resistance—

1. The bar continues to burn for more than  $\frac{1}{4}$  min. after the removal of the flame.
2. The bar does not burn for more than  $\frac{1}{4}$  min. after the removal of the flame.
3. The bar does not catch fire in the flame.

### Electrical Tests

#### *Surface Resistance.*

The surface resistance is measured on a surface of  $10 \times 1$  cm. at 1,000 volts direct electric tension.

$\alpha$ , in the condition as received, but after grinding off the outer surface.

$\beta$ , after exposure to water for 24 hours.

$\nu$ , after exposure to 25 per cent sulphuric acid for three weeks.

$\delta$ , after exposure to ammonia vapour for three weeks.

In tests  $\beta$  to  $\delta$ , any percentage alteration in the weight of the sample caused by the action of the liquids and gases is to be noted.

In order to determine the surface resistance, two straight

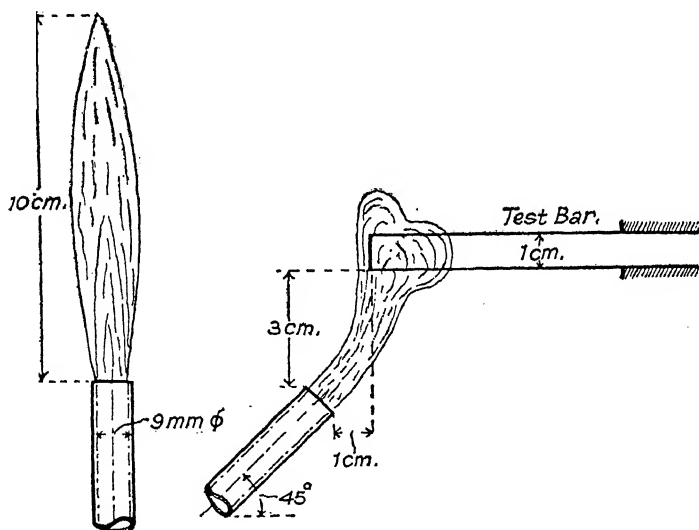


FIG. 18

electrodes 10 cm. long, coated with india-rubber and tin-foil, are placed on the plate in parallel at a distance of 1 cm. (See the standard apparatus, Fig. 19.) The electrical connections are shown in Fig. 20. One electrode is connected through a protective resistance of 10,000 ohms with the negative pole of the 1,000 volts direct voltage, the positive pole of which is earthed; the other electrode is connected with one terminal of the galvanometer shunt circuit, the other terminal of which is earthed. In order to eliminate the effect of stray currents

the connection to the shunt circuit, and from there to the galvanometer is provided with an earthed sheath. The supporting plate for the electrodes must be earthed, and the galvanometer and its shunt circuit must be placed on earthed supports; the sensitivity of the galvanometer must be at least  $1 \times 10^{-9}$  amp. per 1 mm. deflection at a scale distance of 1

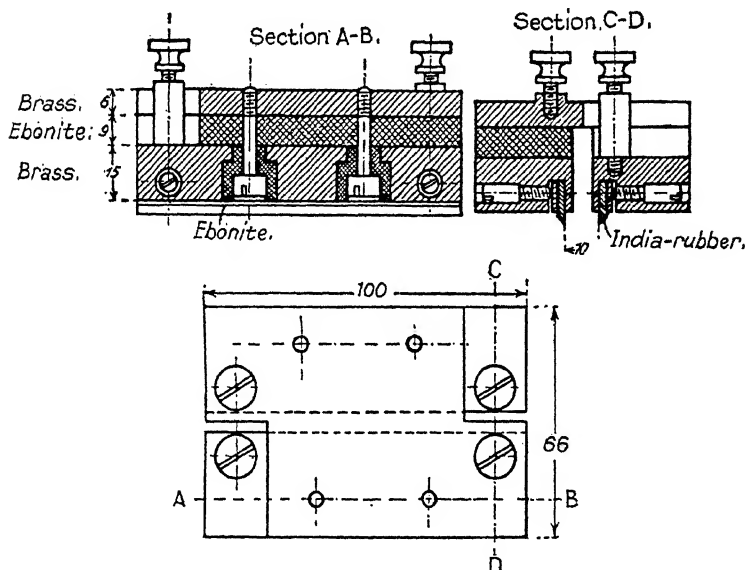


FIG. 19

metre, and the shunt circuit must enable the sensitivity to be decreased step by step to  $\frac{1}{10}$ ,  $\frac{1}{100}$ ,  $\frac{1}{1000}$ ,  $\frac{1}{10000}$ , and  $\frac{1}{100000}$ . One contact of the shunt circuit also serves to short-circuit the galvanometer; in order to calibrate the galvanometer deflections, a coil resistance of 1 megohm is connected with shunt circuit  $\frac{1}{10000}$  in place of the surface resistance apparatus. This coil resistance is wound unifilar with manganin wire of 0.05 mm.

diameter, and need not be adjusted with an accuracy exceeding 3 per cent. The protective resistance consists of manganin wire of 0.1 mm. diameter, wound unifilar on a tube of porcelain or glass, of about 6 cm. diameter and 50 cm. long; the protective resistance must also be adjusted with an accuracy of 3 per cent. The voltage behind the protective resistance is measured by a static voltmeter.

**Method of Testing.** With switch open between the protective resistance and the surface resistance apparatus, the direct

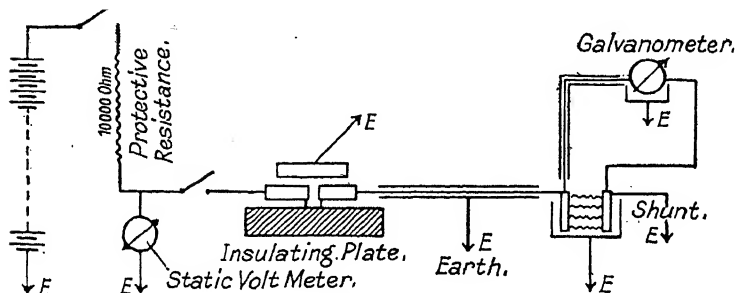


FIG. 20

voltage is adjusted to 1,000 volts with the aid of the static voltmeter. The switch to the surface resistance apparatus is now closed, the galvanometer being short-circuited; should the voltage at the voltmeter then be below 500 volts, the surface resistance of the insulating material is below 10,000 ohms; if this voltage is still over 800 volts, measurements may be made with the galvanometer.

The galvanometer deflection is read 1 min. after applying the voltage.

The reference figures decrease as follows—

Surface Resistance	Reference Figures
Below 1/100 . . .	0
1 to 1/100 . . .	1
100 to 1 . . .	2
10,000 to 100 . . .	3
1,000,000 to 10,000 . . .	4
Over 1,000,000. . .	5

Three plates are to be used for each series of tests, and at least two measurements are to be made on each plate. The plates used for test  $\beta$  may be further used for test  $\gamma$ .

Test  $\beta$ . After removal from the water the plates are rubbed with a cloth, and placed vertically in still air at room temperature for two hours, in order to remove externally adherent moisture. The test is then carried out.

Test  $\gamma$ . After removal from the sulphuric acid, the plates are rinsed for about 1 min. in running water and then treated as for test  $\beta$ .

Test  $\delta$ . The plates are suspended in large glass vessels on the floors of which saturated aqueous ammonia solution is placed, and the vessels are then closed by glass plates. Every three days a little ammonia solution is added in order to replace the losses of ammonia vapour. After removal from the vessels the appearance of the plates is noted, after which they are wiped with a cloth and tested.

**Internal Resistance.** Two holes of 5 mm. diameter and with a distance of 15 mm. between centres are to be bored into the plate to about two-thirds of its thickness and filled with mercury. The resistance between the two mercury electrodes is determined at 1,000 volts direct voltage; should this be lower than the surface resistance as determined by test  $\alpha$ , the plate must be turned down to deeper layers, and the surface resistance measured immediately after this has been done.

**Arc Resistance.** The plate is laid horizontally, and two pure arc carbons of 8 mm. diameter are placed on the plate at an angle one to another of rather more than a right angle, and inclined to the horizontal by about  $60^\circ$ . A voltage of about 220 volt is applied to the carbons with a series resistance of 20 ohms. After an arc has formed between the carbons, these are drawn apart at a rate not exceeding 1 mm. per second. The following four degrees of resistance to the action of the arc are then distinguished—

1. The arc can be drawn out to a length of more than 20 mm., and below it a conducting track is formed from the insulating material, which remains conductive after cooling.

2. The arc can be drawn out to a length of more than 20 mm.,



and a conductive track is formed below it from the insulating material, but this track loses its conductivity on cooling.

3. The arc can be drawn out to a length of more than 20 mm., but no continuous conductive track is formed in the insulating material.

4. The arc cannot be drawn out beyond its normal length of about 20 mm.

### NOTES ON THE REGULATIONS FOR TESTING INSULATING MATERIALS

The regulations refer to tests on insulating materials in specially shaped normal test pieces. The tests serve to determine the quality of the actual material of which the pieces are composed. By standardizing certain testing methods it is possible to determine and to record in an unambiguous and reproducible manner certain important properties of an insulating material, although these are not physical constants. The manufacturer of the material can thus control the quality of his product and uniformity of its production; the data regarding its properties enable the user to select an insulating material suitable to his requirements.

Insulating materials which are to be subjected to press-moulding, however, produce finished insulator parts, the specific properties of which, and more especially the mechanical properties, vary more or less considerably, according to the shape of the part in question, from those of the normal test bars and plates, produced from the same material; varying results will also be obtained at various points of the same insulating part. The examination of an insulating material cannot, therefore, supply direct data for the calculation of the proper shape and dimensions of an insulating part, for defining conditions of acceptance for such parts, as is the case with numerical data obtained with a completely homogeneous constructional material. Therefore an examination of the material in the form of normal test-pieces does not suffice, and must be supplemented by an examination of the finished insulating part in the form in which it is to be used, in order to determine whether the selected insulating material is satisfactory in this particular

form. The principles for regulations for the testing of parts are at present in process of development by the testing station for finished insulating parts, established by the V.D.E. at Nürnberg.

The present regulations for testing the material therefore supply a portion only of the total requirements. The regulations include those tests only which are absolutely necessary for the characterization of the insulating material. They were selected from a very much greater number of tests which were carried out by the Material Prüfungsamt (Testing Institute for Materials), and by the Physikalisch-Technische Reichsanstalt (the Imperial Physical-Technical Institute, Charlottenburg), for the purpose of establishing the principles of such an examination. (Passavant, *E.T.Z.* (1912), page 450.) For many purposes further tests will be necessary than are prescribed in the Regulations, for example, the breakdown voltage for insulating materials at voltages exceeding 750 volts. In such cases, adherence to the conditions of the further tests in the article referred to is recommended.

## GENERAL NOTES

### *Form of Test-piece.*

The main factor in deciding the dimensions of the test-pieces was that some insulating materials cannot be produced of thickness below 10 mm. The bar form is the most suitable for the mechanical tests; it was first intended to use plates for the electrical tests, but as the bars proved more suitable in this case also, these were accepted as the normal form for the whole examination. It was not advisable to cut bars out of a plate, as some press-moulded materials cannot be cut satisfactorily, and the mechanical properties may be partly dependent on the press-moulded outer skin.

The breadth and length of the bar were so chosen that the bending load in kilograms per square centimetre, according to test, was ten times as large numerically as the load in kilograms.

## Mechanical Tests

The purpose of the mechanical tests is to reproduce, as far as possible, the conditions to which the insulating

material is exposed during use, namely, bending, impact and pressure.

### *Bending Strength.*

The bending stress  $\sigma_b$  is the ratio of the bending moment  $M$  to the moment of resistance  $W$ . If a force  $P$  is applied in the middle of a test bar resting on two supports, at a distance  $l$  apart, the bending moment is  $M = \frac{Pl}{4}$ , where  $b$  is the breadth and  $h$  the height (i.e. thickness) of the bar in cms.; if the chosen dimensions are exactly complied with, namely,  $l = 10$  cm.,  $b = 1.5$  cm., and  $h = 1$  cm., then  $\sigma_b = 10P$ , in kg. per sq. cm.

The regulations first proposed provided for graduated application of the load in steps of about 150 kg. per sq. cm., which were to be applied to the test bar for 2 min. It was intended that these steps should serve as degrees of quality for classifying the insulating materials, but they proved too far apart for practical requirements, and, therefore, smaller increases in the load were prescribed in the regulations of April, 1922. However, once the degrees of quality had been abandoned the step-wise increase of the load had no further definite justification, and the alteration was made of increasing the load continuously until rupture occurred, as is the general custom in determinations of mechanical strength. The operation is then more convenient, requires less time, and gives the exact breaking load. In order to eliminate the effect of varying rates of load increase, a definite rate was prescribed, namely, 250 kg. per sq. cm. per minute, which results in a duration for the test of about 1 min. for a material of average strength. If information regarding the delayed effect is desired from the bending test, the test can be repeated with larger or smaller rates of load increase. A sufficient indication of the delayed effect is, however, provided by the test, Ball Hardness, in which the depth of impression is measured after two different durations of the load.

Of the chemical influences to which the insulating material may be exposed in practice, those of mineral oil, acids, and caustic alkalies are the most frequent.

The action of mineral oil can only be gauged by the mechanical tests, but that of acids and caustic alkalis influences the electrical surface resistance of the insulating material much more than its mechanical strength, and the effect in these cases is therefore determined by the electrical tests,  $B_1$ ,  $\gamma$ , and  $\delta$ .

### *Impact-bending Strength.*

The determination of the impact-bending strength serves to evaluate the brittleness of insulating materials, i.e. their resistance to a percussive load.

The pendulum impact apparatus hitherto used, of 150 cm.-kg. energy output, was adapted for use with the hardest insulating materials, such as laminated paper, and so forth. It has been found advisable to test the less resistant materials with lighter pendulum impact apparatus, in order to be able to differentiate more easily by means of smaller impact loads. At the request of the Commission for Insulating Materials, the firm of Louis Schopper, Leipzig, constructed the pendulum impact machine represented in Fig. 21, which is provided with two interchangeable pendulums of 10 and 40 cm.-kg. energy output.<sup>1</sup>

The supplying firm have given us their permission to publish the following main numerical data—

	10 cm. kg. Pendulum	40 cm. kg. Pendulum
Angle of elevation . . . . .	160°	160°
Total weight of swinging part . . . . .	304 gm.	1020 gm.
Distance of centre of gravity from axis of pendulum . . . . .	169.2 mm.	202 mm.
Distance of fall of centre of gravity . . . . .	328.3 mm.	391.8 mm.
Distance of centre of blade from axis of pendulum . . . . .	225 mm.	225 mm.

The 10 cm.-kg. pendulum is used for ordinary pressed insulating materials, and the 40 cm.-kg. pendulum for ebonite. The apparatus is provided with supports, both for normal bars

<sup>1</sup> The photograph used for Fig. 21 was kindly placed at our disposal by the firm of Louis Schopper, Leipzig.

and for bars of  $5 \times 10 \times 60$  mm. The 150 cm.-kg. pendulum is used for materials of extreme strength only.

It is important to place the apparatus in an accurately vertical position on a sufficiently rigid support.

On lifting the catch *K*, Fig. 21, the pendulum swings down from its initial elevation of  $160^\circ$ . It hits the sample at its

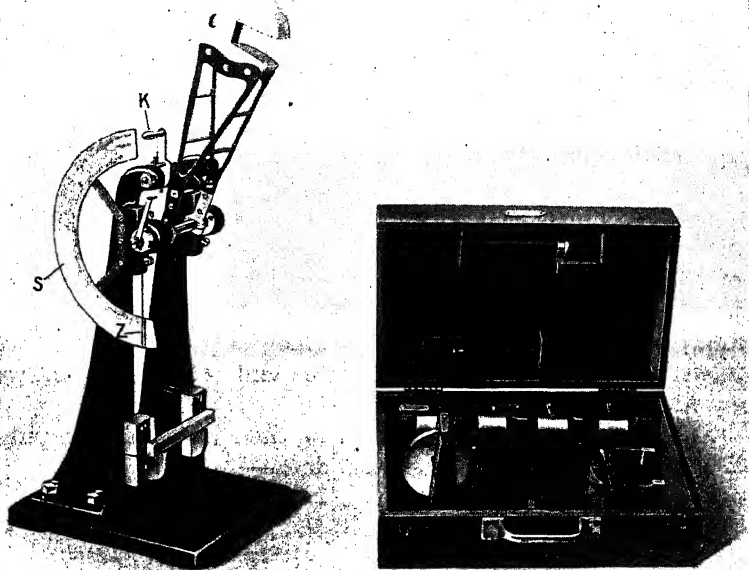


FIG. 21

lowest position, and after breaking it swings through to the other side of the apparatus. The magnitude of the upward swing is read in degrees of angle on the scale *S* by means of the indicator *Z*. From this reading the energy content of the pendulum after breaking the test bar can be calculated. The difference between the angles of fall and of ascent, together with the total energy of the pendulum, give the energy absorbed by the impact on the sample. The friction of the pendulum and the indicator is allowed for in the graduation of the scale which

indicates the angle of ascent for the 10 and 40 cm.-kg. pendulums, so that special deductions for the loss through these causes is not required.

It is advisable to ascertain occasionally whether the degree of friction of the ball-bearing and of the indicator has altered, but if the apparatus is maintained in good condition such variations scarcely occur. As the work performed is not proportional to the angles, but to the heights of fall, it is advisable to construct a curve in order to be able to read off the actual energy absorbed by the impacts.

The brittleness usually increases with fall of temperature, and an additional impact bending test in the cold is, therefore, prescribed for materials intended for use in the open. The temperature of about  $-20^{\circ}\text{C}$ . can be obtained by a mixture of coarse salt and ice in the proportions of 1 : 2 to 1 : 1. It is most important to be certain that the samples actually acquire this temperature; this is most reliably achieved by immersing them in the actual freezing mixture for about 20 min. Each sample is removed from the freezing mixture immediately before the test, contact between the hands and the middle of the sample being avoided as far as possible, freed quite superficially from the adherent liquid and tested as rapidly as possible.

### Ball-hardness

Various processes may be employed for determining the resistance of a material to compressional loads. The ball pressure process adopted in this case serves to determine not only the actual resistance to pressure, but also the hardness by the so-called penetration method.

According to earlier regulations, a 5 mm. ball of glass-hard steel was pressed into the sample to a depth of 0.1 mm., and the hardness measured by the force required to produce this degree of penetration. In course of time it was found that this method is not very suitable for testing insulating materials, as many of these show very marked delay effects, so that smaller or larger forces are required in order to produce a given penetration, if the force is more rapidly or more slowly applied;



on a loaded beam, resting on the fixed points  $B$  and  $C$ , and loaded with weights  $P$  at the overhanging ends  $A$  and  $D$  at distances  $a$  from the points of support. The bending moment increases from  $A$  to  $B$  and from  $D$  to  $C$ , attaining a maximum  $M = G.l$ , which remains constant along the whole distance between the points  $B$  and  $C$ . At the test-piece the moment  $G.l$  corresponds to the moment  $P.a$ , so that  $M = G.l = P.a$ . It is advisable not to use too small a lever arm  $a$ , for the force  $P$ , so that  $P$  may not become too large and so cause local impressions on the sample. Within wide limits the length  $b$  is immaterial. The error caused by the fact that the fall of the lever  $H$  and lateral displacement of the sample causes an alteration in the bending moment,  $G.l$  becomes no longer negligible if  $b$  is too large. The dimensions of the normal test-bar and of the normal apparatus, however, lead to a satisfactory dimension for  $b$ . If  $l$  is not made too small, so that  $G$  is not too large, the compressional force acting vertically along the bar also becomes negligible. For the sake of simplicity, we have so far assumed the acting moment to be equal to  $G.l$ ; in actual fact it is, of course, necessary to add the amount of the moment due to the weight of the lever  $H$  itself; the actual moment acting on the test-bar is, therefore,  $M = G.l + H.l = P.a$ .

As was established by later tests, the rate of temperature rise of 125–150° C. per hour, which was formerly prescribed, led to an unsatisfactorily large difference between the temperatures of the test bars and those of the air oven in which they were enclosed. The rate of temperature rise has, therefore, been reduced to about 50° C. per hour, as in this case the temperature difference between test-bar and oven is not more than 5–6° C.

The heat sources must be so arranged that the test-bars are heated uniformly throughout their lengths. Experience has shown that if this requirement is neglected, inconsistent results are obtained.

When several Martens instruments are housed in one oven, thin partitions must be introduced between the individual levers, and spring-catching devices must be provided so that the fracture of one sample does not interfere with the adjoining



tests. No regulations have been prescribed regarding the construction of the ovens or indicators to show the dropping of the levers, in order that any available ovens might be used; it is, however, important to ensure that the samples are heated uniformly, and that the measurement of the position of the lever is not rendered inexact by displacement of the zero point during heating. In order to facilitate rapid adjustment of the position of the load, in accordance with the inevitable variations in the moments of resistance of the test-bars, it is advisable to provide a suitable scale on the lever arm.

### Fire Test

The test was devised in accordance with the definition of fireproofness in the Erecting Regulations. The position of the burner, inclined at an angle of  $45^{\circ}$  and slightly removed from the sample, was chosen in order to prevent fouling of the burner by any softened products which might fall on it off the test-bars.

The test for fastness to frost has been omitted in the new regulations, as deficiencies in this respect are entirely due to water contents, or absorption of water, and such absorption is much more certainly detected by the electrical tests.

### Electrical Tests

*Test B1.* The conditions which insulating constructional materials for apparatus and installations have to withstand do not necessitate electric strength, i.e. electrical breakdown resistance, to any serious degree, the only requirement being that the material shall not be appreciably conductive. A large number of materials are excellent conductors in a perfectly dry condition, but many of these become electrolytically conductive and, therefore, useless in the presence of moisture. This is naturally most immediately and most strongly observable at the surface of the insulating material; therefore from an electrical standpoint an insulating material is sufficiently characterized for this purpose by its surface resistance under various conditions.

Frequent attempts have been made to improve insulating

materials which are not moisture-proof by applying a water-tight coating. Apart from the fact that, in practice, these thin coatings are easily damaged and their protective powers thus rendered questionable, in this case the materials themselves must be tested and characterized, and not any possible coating; hence, the regulation that the surface of the plates shall be removed by grinding before testing.

The resistance measured by the prescribed standard apparatus is not actually the surface resistance only, as the effect is shared by the interior of the insulating material, because the electric lines of force between the two blades which carry the voltage, do not run entirely along the surface, but also within the material. The conditions are, however, usually quite similar in the case of an insulating material in actual use. As all particulars of the apparatus and method of testing are quantitatively prescribed, the results are entirely unambiguous; the expression of the measured resistance as "surface resistance" is merely an abbreviation, which uses the name of the main factor involved.

The test-plate must not be placed on an earthed metallic surface during the test, as the distribution of the electric field is thus altered and may lead to too high a result for the measured resistance.

The insulation resistance, and especially the surface resistance, has no fixed value, as has, for example, the resistance of a wire, but generally decreases in about inverse proportion to the voltage. A definite measuring voltage had therefore to be prescribed, which had not to be too low in order, on the one hand, not to lead to resistances of too favourable a character for poor insulators, and on the other, in order to enable the best insulators to be recognized. The current strength is limited to 0.1 amp. by the interposed protective resistance of 10,000 ohms, and the current source need, therefore, supply 100 watts only. The most convenient source of current is a small dynamo, the voltage of which is regulated by the exciter, and can be reduced to a few volts only by cutting this out, so that the test-bars may be interchanged without danger. Small accumulators of 0.1 amp. discharge current may also be combined to

form a battery, subdivided into suitable groups for charging; they must be vigorously discharged and re-charged at regular intervals, as the slight discharge which occurs during the tests does not suffice to prevent the positive plates from hardening.

Another method is to transform up an alternating voltage and then to pass this through a rectifier, but care must be taken that the direct voltage so obtained does not pulsate too much. A three-phase rectifier is greatly preferable in this respect to a monophasic rectifier, on account of the greater degree of overlapping of the voltage half-waves. In all cases special means are necessary to limit the degree of pulsation; this is best effected by loading a capacity  $C$  together with the rectifier. If three-phase current of a frequency of 50 cycles per second is employed, and the direct voltage of 1,000 volts is not to fluctuate more than 5 per cent when the current consumption through the surface resistance apparatus is  $i$  amp., then  $C$

must equal  $1.3 \times 10^{-1}$  micro-farads. When  $i = \frac{1}{10}$  amp.,  $C$  would therefore be 13 micro-farads; but for many values it would be sufficient to measure the surface resistance with a lesser degree of accuracy, for example, below 1 megohm (the limit between comparative numbers 1 and 2); for  $i = 0.001$ , the capacity  $C$  would have to be 0.13 micro-farads. Such a condenser for 1,000 volts direct voltage is easily constructed. For measurements of resistances of more than 10 megohms the pulsations would then be imperceptibly small.

Instead of a condenser a resistance (but not a throttling coil) may be interposed, which does not absorb too small a current, for example, 0.5 to 1 amp., and from which the voltage is diverted for measurement; by means of a throttling coil in front of the resistance the pulsations of the current through the resistance can be weakened. The working of this arrangement, however, absorbs considerable quantities of energy.

In the measurement of the surface resistance the exact magnitude is not important, but merely the order of magnitude. The degrees of magnitude, starting from  $\frac{1}{100}$  megohms,

are successively multiplied by 100, and designated by reference numbers.

Among chemical influences, the attack by acids or alkalis is markedly reflected in the surface resistance result. In order to shorten the test, the most commonly occurring effects of this character have been selected; dilute sulphuric acid, which is distributed everywhere in accumulator sheds by the gases evolved from the cells during charging, and ammonia, which is evolved in cattle-sheds and similar places. As the attack cannot be accelerated, the duration of the test had to be prescribed as three weeks.

*Test B2.* In insulating materials containing synthetic resins it sometimes happens, in consequence of incompleteness of the process of production, that water is liberated within the mass, whilst the surface shows excellent insulating properties. In order that such defects might be detected, the measurement of the internal resistance was added to the revised regulations.

*Test B3.* The position of the carbons in the arc test is so chosen that the hot gases rising from the arc can freely escape in an upward direction. An insulating support, carrying two horizontal round iron bars in a straight line, is attached to a stand. A block slides along each bar, and is provided with a boring inclined at rather more than  $45^\circ$  to the length of the bar. A carbon arc electrode is clamped into each boring, and projects to such an extent that the plane containing both electrodes is inclined at about  $60^\circ$  to the horizontal. The current leads are connected to the blocks by terminal screws. After the arc has been struck, the one block is slid along its iron bar at the prescribed velocity, whilst the other block remains stationary.

The resistance to the arc is classified according to the degree to which the insulating material assists, permanently or temporarily, in the passage of the current, owing to the influence of the arc. According to the new form of the regulations the four various characteristic cases are arranged in sequence, and denoted by 0, 1, 2, and 3 as degrees of resistance to the action of the arc. The causes of the varying behaviour are the following.

1. The insulating material carbonizes, and the carbon so formed conducts the current even after cooling, so that the arc is re-started.

2. The insulating material is converted into so-called conductors of the second class (such as the filament of a Nernst lamp), which conduct the currents whilst red-hot, but not when cold.

3. Combustible gases are evolved from the insulating material, which enable the arc to be extended beyond the normal length of 22 mm., but the insulating material does not itself become conductive.

*Directions of the V.D.E. for the Testing of Insulating Parts  
for (Electric) Installations.<sup>1 2</sup>*

(Draft. Not yet Final.)

V.D.E. 315

**Introduction.** Various sections of the "Regulations for the Construction and Testing of Material for Electric Installations" prescribe properties, without explaining how these are to be determined. For example, fire-proof, heat-proof, and moisture-proof properties are demanded, and their meaning defined. It is also demanded that insulating parts which come into contact with an arc shall be fire-proof, and mechanical resistance is also required. Moreover, the insulating property of a finished apparatus after lying in "moist air" is to be confirmed.

In no case, however, are explanations provided as to the means by which these properties are to be investigated, and as to what the testing methods and results should be. Moreover, no particulars are anywhere given regarding temperatures, and so forth. Many testers of such material, therefore, held the view that the "directions for the examination of electrical insulating materials" were authoritative for the determination of the properties of insulating bodies.

The Commission for (Electrical) Installation Materials empowered two sub-commissions to regularize the position and

<sup>1</sup> The reproduction of these directions, which are at present available in draft form only, is due to the kind permission of the V.D.E.

<sup>2</sup> See *Elektrotechn. Zeitschr.* (1924), 1389.

devise regulations, the one for Insulating Bodies (Chairman, Director Schneider, Frankfurt a.M.), and the other for Testing (Chairman, Prof. Edelmann, Nürnberg).

It was first decided that an examination according to the "directions for the examination of insulating materials" was unsuitable, and that the examination of finished insulating bodies must be effected by other methods. It was decided that the sub-Commission for Insulating Bodies must draw up tables, showing what requirements each individual article must fulfil, in accordance with its application, but these tables could only be produced after decisions had been arrived at regarding the methods of testing.

The directions published herewith, which were produced by the sub-Commission for Testing, and accepted by the Main Commission for Electrical Installation Materials, are published in the interests of the work at the testing station of the V.D.E., and at the testing laboratories which carry out examinations of electrical installation material for the purpose of granting the test marking, without waiting for the completion of the table of specifications.

The following gentlemen were mainly concerned in drawing up the present directions: Edelmann, Grünwald, Hermann, Klement, Molly, Paulus, Ruppel, Schiff, Schneider, Schoof, Zimmermann.

The present draft is intended to form a temporary basis for tests and reports, until final regulations can be produced as a result of further work and experience. In the interest of such work, it is requested that any experience in these directions which might be of use in establishing final regulations should be sent as soon as possible to the office of the sub-Commission. The construction of the apparatus has been undertaken by the firm of H. Unbehauen, Berlin, No. 18, Weberstrasse, 5.

## GENERAL

*Purpose.* The directions are intended to supplement the "Regulations for the Construction and Examination of (Electrical) Installation Materials" with regard to the examination

of insulating bodies. It is intended that they should ultimately be converted into regulations.

*Definitions.* (a) Directly insulating bodies are carriers of parts under electric tension and other bodies which are in direct contact with parts under electric tension.

(b) Indirectly insulating bodies are covers, linings, and so forth, not included under (a).

### Conduct of the Tests

According to the Regulations for Erection, and the "Regulations for the Construction and Examination of Electrical In-

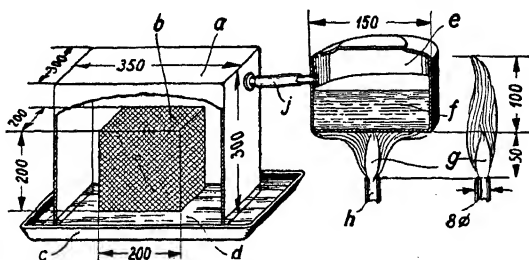


FIG. 23

stallation Material," the qualities of insulating bodies to be investigated include—

- (a) Resistance to moisture.
- (b) Mechanical resistance.
- (c) Heat resistance.
- (d) Resistance to fire.

*Resistance to Moisture.* The cover-box *a* in Fig. 23 (350 mm., 300 mm., 300 mm.) stands on a tray *c* (400 mm., 400 mm., 40 mm.), which is filled with water to a depth of about 20 mm. The space available for the test shall measure 8 cu. dcm. Steam is admitted to the cover-box from a boiler *e*, of about 2 litres capacity, the water-contents of which before the test should be about 1 litre. The tube aperture of the Bunsen burner *h* should be 8 mm. The height of the flame, at a gas pressure of about 50 mm., must be 150 mm., the height of the core of the flame being 50 mm. An india-rubber tube *j* may be used to connect the boiler *e* with the cover-box *a*.

### Conduct of the Test

*Efficiency after Prolonged Action of Steam.* The test object must be placed in the cover-box, mounted in the manner as actually used, and steam is to be introduced for 1 hour. It is then to be left in the closed cover-box for at least 11 hours, without any previous change of the atmosphere in the cover-box. Electric tests must then be carried out without removal of water-drops, and so forth. The water remaining in the boiler after the test should amount to about 0.4 litres.

*Efficiency in Moist Air.* As in Test 1, but steam is to be supplied for 6 min. only, and the sample allowed to remain in the cover-box under the same conditions for 12 hours. The water remaining in the boiler after the test should be about 0.96 litres.

*Efficiency in a Room Atmosphere.* As in Test 1, but without steam supply, the water in the tray being sufficient.

*Results of Test 1 to 3.* The insulating bodies must satisfy the following respective tests—

Test according to par. 11 for switches;		
„	„	20 for plugs, sockets;
„	„	29 for safety elements (fuse units);
„	„	43 for sockets;
„	„	48 for hand-lamps;

and suitable tests for other articles.

NOTES. The above-mentioned paragraphs of the “Regulations for the Construction and Testing of Electrical Installation Material,” specify that the insulation after exposure to moist air for at least 12 hours must withstand a testing voltage of 1,500 to 2,500 volts for 1 min. without any arcing. No statement was issued regarding the determination of moisture of the air, which should be included in this test. The ordinary simple methods of determining the moisture are so inexact, that even with identical forms of apparatus considerable differences might occur in the results obtained. For this reason the process was simplified, by specifying that a definite quantity of water must be evaporated for each determination.



Identity of the tests is, however, only ensured if—

1. The volumes correspond to those specified.
2. The evaporated quantities of water are those specified.
3. The volume of the bodies to be investigated simultaneously is not greater than the volume specified.

Otherwise it might happen that the surface of the bodies under investigation was so large that an insufficient quantity of condensed moisture was produced per unit of surface. After remaining in the cover-box, the test objects must be submitted to the test voltage specified in the above-mentioned paragraphs without removal of the surface moisture.

*Mechanical Resistance.* The investigation of mechanical resistance must be carried out in accordance with practical requirements. The following tests are required—

1. Tests for the holders of portable lamps.
2. Tests for the covers of revolving switches and plugs and sockets.
3. Tests for other articles.

### Tests for the Holders of Portable Lamps

A stand is provided (Fig. 24) with an anvil rail  $d$  of angular cross-section. At a distance of 1,000 mm. from this anvil rail a pivot  $e$  is provided, to which the lead of the lamp is attached by a clamp or otherwise. A release  $f$  is also provided, which enables the lamp to be allowed to fall, without receiving any impulse. The anvil rail must have a radius of curvature along the line of impact of 5 mm.

### Conduct of the Test

The hand-lamp is to be furnished with a correspondingly long lead of the type actually to be used. The socket is to be attached and safety clip provided. The lead is to be attached to the pivot. Three blows are to be imparted, and the apparatus is to be so adjusted that these are received at the points  $a$ ,  $b$ , and  $c$  in that sequence.

*Results of Test.* The holder of the hand-lamp must withstand

these three impacts without damage. Dents are not to be considered as damage.

NOTES. The method of testing was devised in accordance with the working conditions, which the articles must be sufficiently strongly constructed to withstand. The weight of the hand-lamp, including protective cage and other auxiliaries, exerts its full effect, as does also the position of the centre of

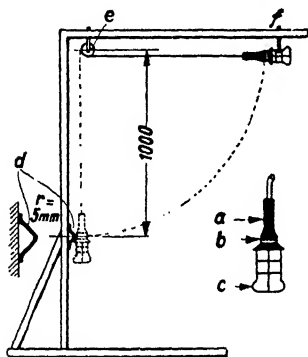


FIG. 24

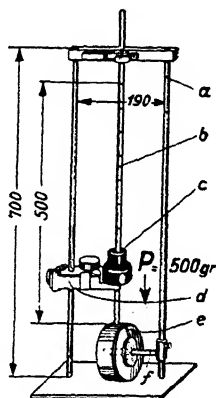


FIG. 25

gravity. The height of fall provided, and the angular form of the anvil rail, serve to test the object sufficiently.

### Tests for the Covers for Revolving Switches and Plug-sockets

The height of fall of a 500 grm. falling weight is adjusted by means of a platform *d* (Fig. 25), attached to the frame *a* of the apparatus, which also supports a guide-rod *b* down which the falling weight slides; the height of fall is adjusted according to the equation:

$$\text{Weight of cover in gms.} = \text{height of fall in cm.}$$

The cover to be tested is held in position by a contrivance of wood or the like (*f*).

### Conduct of the Test

The falling weight is to be dropped once on to the cover from the adjusted calculated height.

*Results.* The covers must resist this treatment without showing any crack or other impression.

*NOTES.* This test provides for the fall of the cover, which may occur during assembling. The various other possibilities of breakage could not be provided for, as the possible accidents to mounted switches are of very varied character.

The method of testing reproduces the impact which would result from a fall of 1 metre, and substitutes for the indefinite direction of fall of the cover, that of a controlled falling body, the weight of which is 500 gm. for covers, the weight of which does not exceed 250 gm. The impact of the weight must be so arranged that it comes into axial contact with the surface of the cover across the whole available height of the cover. From the weight of the cap itself and the weight of the falling weight (500 gm.), the formula

$$\frac{\text{Weight of cover in gms.}}{5} = \text{height of fall in cms.}$$

is deduced.

In order to facilitate the measurement of the height of fall, the guide-rod of the contrivance is to be placed on the rim of the cover, and the height measured on the scale on the guide-rod. The cover must be held by a suitable contrivance in order to prevent it from rolling away. A suitably shaped wooden block, for example, may be used for this purpose, which holds the cover from below by not more than one-third of its circumference. Impact should occur at an unweakened point of the circumference of the cover.

### Heat Resistance of Solid Insulating Bodies

*Apparatus.* The test samples are to be placed in a thermostat (Fig. 26), consisting of a bed-plate, heater, and covering plate. They are to be fastened to special contrivances, without alteration of their shape, and subjected to the action of a load by means of a special device. The weight of the load must be equal to the weight of the object, but not less than 100 gm.

### Conduct of the Tests

1. Resistance for temperature range, 250° C.  
The temperature is to be raised by 50° C. per hour. Final temperature, 250° C.
2. Resistance for temperature range, 150° C.  
As for temperature range, 250° C.; final temperature, 150° C.
3. Resistance for temperature range, 100° C.  
As for temperature range, 250° C.; final temperature, 100° C.
4. Resistance for temperature range, 70° C.  
As for temperature range, 250° C.; final temperature, 70° C.
5. Resistance at temperature range, 50° C.  
As for temperature range, 250° C.; final temperature, 50° C.

*Results.* No noticeable general alteration of shape must be produced during the test. The degree of bending at the loaded lever must be less than 3 mm.

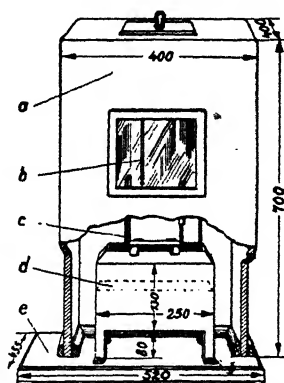


FIG. 26

*NOTES.* The method of testing the mechanical resistance of insulating bodies at raised temperatures usually employed hitherto, was to place the body in a thermostat, the temperature of which was raised to the required point within a specified time. After this temperature had been attained the body was removed from the thermostat, and an investigation was then made with screwdrivers and similar tools as to whether the surface of the body could be deformed. The result was dependent on many uncertain factors; these have now been eliminated. The bodies remain in the thermostat throughout the test, and the result is observed in the thermostat.

The form of the thermostat is of no consequence. A simple form of apparatus, for use up to temperatures of about 180° C., which works reliably and can be cheaply constructed, is shown in Fig. 26.

The test objects, such for example as are shown in Figs. 27, 28, and 29, are placed in this thermostat (together with the testing devices.)

Fig. 27 shows a device for subjecting a cover for switches or plug-sockets to a load.

The parts are indicated as follows—

- a.* Heater of the thermostat.
- b.* Angle-iron support.
- c.* Measuring device.
- d.* Sample under examination.
- e.* Loading device.
- f.* Thermometer.
- P.* The loading weight.

Fig. 28 shows similar devices for plug-sockets and switches, and so forth, and also for plugs.

Fig. 29 shows a device for testing portable lamp sockets, The parts are as follows—

- a.* Socket of portable lamp.
- b.* Holder for same.
- c.* Measuring device.

*P.* Indicates the loading weight which is to be used in place of the safety glass and cage, if these are not used during the test. A weight of 500 gm. generally suffices for ordinary hand-lamps.

In Fig. 26 the parts are designated as follows—

- a.* The thermostat cover.
- b.* Thermometer.
- c.* Loading device.
- d.* Heater.
- e.* Ground plate.

It is a fundamental condition of the tests that no alteration of shape must be made before or during the test; thus, for example, no holes must be made in order to affix testing devices. Thus, for example, a cover for switches or plugs must be attached to the holder of the contrivance by means of its normal

perforations. A clamp is affixed to the rim of a cover, which also supports the load. The leverage for the weight is to be arranged in the proportion 1 : 5, so that if the clamp on the

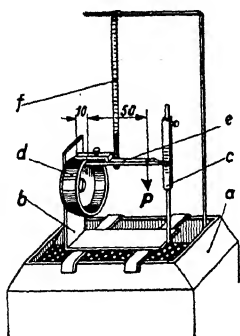


FIG. 27

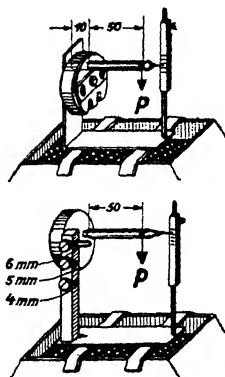


FIG. 28

cover is 10 mm. long, the weight must be attached 50 mm. distant from the edge of the cover. The weight should be equal to the weight of the object under test, but not less than 100 gm. The investigation of sockets, plugs, or portable lamp-holders is carried out in the manner indicated in Figs. 27 and 29.

It has already been mentioned in the directions that no appreciable change of shape should occur during the test, and that the displacement of the loading lever must not exceed 3 mm.

The above-mentioned temperature ranges apply to articles intended for use in normally heated spaces only. Other testing temperatures have naturally to be employed for articles intended for use in hot spaces, and these have still to be decided.

NOTE. The temperatures at present usual for testing the following objects are—

1. Safety and cover lids, 70° C.

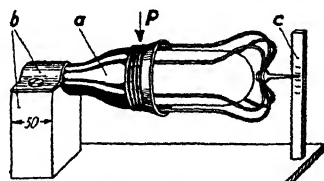


FIG. 29

2. Supports for parts under electric tension, 100° C.
3. Portable lamp-holders, 150° C.
4. Parts for cut-outs, 250° C.

The question is at present being investigated as to whether safety covers which are heat-proof at 50° C. suffice for general purposes.

### Heat Resistance of Compositions

Compositions serve to cover, but not to support, parts under electric tension.

*Apparatus.* (Fig. 26.) The test objects are to be placed in the thermostat in the position in which they are to be used.

### Conduct of the Test

The temperature is to be raised to 70° C. within 1 hour.

*Results.* No alteration in the position must occur during the test.

NOTE. Compositions should resist practical conditions without change of position. In order to control their behaviour, composition articles, such as switches, plug-sockets, and cut-outs, are placed in a thermostat in the same positions as when in use. The temperature in the thermostat must be raised to 70° C. within an hour. At the end of this period the compositions may have softened, but no change of position must have occurred. Compositions containing paraffin wax and similar materials are therefore not permissible.

### Fire Resistance

Directions are being prepared.

The Association of German Electrical Engineers is preparing further V.D.E. regulations on insulating materials, and it may be assumed that these will be accepted during the year 1929-1930. Meanwhile, pamphlet V.D.E. 427 has appeared on the Examination of Insulating Tapes.

# INDEX

- ABONYI, 395  
 Absorption spectra, 71  
 Acetaldehyde, 85  
 Acetone, 304, 366  
 Acetylene, 83  
 Acid resins, 119  
     — tars, 119  
 Acrolein, 103  
 "Acrolite," 194  
 Acrylic acid, 98  
 Aeroplane propellers, 356  
 Agglomeration, 25  
 "Albertol" shellacs, 279  
 Aldehyde resins, 259  
 Aldols, 182  
 Aldoses, 279  
 Aliphatic amines, 159  
 Aliphatic ketones, 105  
 Amber, 4, 7, 337  
 Amberite, 324  
 "Aminoplast," 160  
 Ammonia, 391  
 Aniline, 129  
 Anthracene, 202, 209  
 "Antioxygen," 191  
 Antiseptic paints, 372  
 Aralkyl halides, 210  
 Arsem, 199  
 Artificial asphalts, 50  
 Asbestos, 358  
 Asphalts, 18  
 Association colloids, 43  
 Autoxidation, 32, 48  
 Azomethine group, 66, 126, 131  
  
 BAEKELAND, 10, 148, 155, 180, 294.  
     309, 339  
 Baeyer, 273  
 Ball-hardness, 425  
 Bakelite, 324, 332  
 Barthélemy, 148  
 Beckurtz, 288  
 Bemmelen, 195  
 Bender, 151, 155, 180  
 Bending strength, 422  
 Bengal lights, 127  
 Benzaldehyde, 124, 192  
 Benzoin resin, 30  
 Benzoin, 182  
 Benzophenone, 25  
  
 Bikanton, 355  
 Billiard balls, 338  
 Binding agents, 407  
 Birkby, 312  
 Bitumens, 18  
 "Bloom," 7  
 Blue earth, 4  
 Blumer, 321  
 Böhler, 126  
 Böhler's resin, 157  
 Brake linings, 356  
 Brock, 307  
 Bromacetylene, 84  
 Bruson, 116  
 Butadienes, 63, 131  
  
 CALLAHAN, 199  
 Cannizaro's reaction, 184  
 Carbide, 229  
 Carbonyl group, 64, 123  
 Carbonyl group, 98  
 Carboxylic acids, 119  
 Carnauba wax, 244  
 Casein, 279  
 Castings, 333  
 Catalysts, 72  
 Cellulose esters, 50, 56  
 Cements, 360  
 Caro, 144  
 Chemical similarity, 41  
 Chewing gum, 249  
 Chinese wood oil, 58  
 Chloroform, 117, 209, 213  
 Cinnamic acid, 100  
 Claisen, 179  
 Claypoole, 314  
 Cold moulding, 340  
 "Collector micanite," 268  
 Colloidal final products, 49  
 Colloids, 74  
 Colophony, 8, 202, 233  
 Colour, 335  
 Comey, 378  
 Condensing agents, 137  
 Conifer resin acids, 32  
 Conjugated carbon double linkages,  
     112  
 Copal substitutes, 364  
 Copals, 3  
 Coster, 143



- Coumarone resins, 9, 11, 241  
 Craven, 281  
 Creosote, 226  
 Cresol, 278  
 Crotonaldehyde, 133, 184  
 Crotonic acids, 100  
 Cresols, 288, 380  
 Crystallites, 55  
 Cumarone, 92, 214, 229, 243  
 Cuprene, 83  
 Cyanic acid, 68  
 Cyclopentadiene, 63, 116  
 Cymol, 187
- DANCCKWORTT, 291  
 Dawson, 200  
 Dekonite, 337  
 Dennis, 239  
 Dentures, 338  
 Dextrines, 18  
 Dianin, 180, 223  
 Dieser, 177  
 Diphenylethylene, 111  
 Disacryl, 104  
 Dixon, 161  
 Döbereiner, 185  
 Door knobs, 360  
 Dreyfus, 188  
 Dubois, 222  
 Dufraisse, 104
- EBONITE, 336, 378  
 Edelmann, 267  
 Eibner, 35, 44, 66  
 Ekeknantz, 186  
 Elasticity, 41  
 Elder, 88  
 Electrical properties, 332  
 — tests, 415  
 Electrolysis, 314  
 Elemi resin, 30  
 Ellis, 165, 169, 220, 236  
 Emery wheels, 345  
 End-products, 38  
 Enzymatic action, 35  
 Estralite, 347  
 Ethine (acetylenic) group, 68  
 Ethereal oil, 31  
 Ethylene double bond, 59  
 — linkage, 87  
 Ethylenic linkage, 62  
 Ethyl-sorbinic, 120  
 Eucalloids, 78
- FACTIS manufacture, 222  
 Fantasite, 408  
 Fillers, 314
- Fillings, 342  
 Fireproof articles, 346  
 — coatings, 361  
 Fischer, 224  
 Fissional acetylation, 75  
 Flint glass, 408  
 Flocks, 21  
 Florida earth, 226  
 Fonvabert, 391  
 Formaldehyde, 9, 141, 156, 159, 162  
 Formaldoxime, 126  
 Formalin, 297  
 Formic acid, 399  
 Franconite, 211  
 Frankenheims, 27  
 Fur-drying, 373  
 Furfurol, 189, 318, 377
- GEAR wheels, 356  
 Gelatinizing capacity, 41  
 Gilsonite, 244  
 Glaser, 232, 236  
 Glass substitute, 362  
 Glycerine, 196, 200, 317  
 "Glyptals," 196  
 Goldschmidt, 162  
 Gramophone discs, 345  
 Grignard, 183  
 Grotthus's Law, 70
- HABER, 20, 24  
 Haitinger, 215  
 Hammarsten, 185  
 Hardening process, 322  
 — resins, 325  
 Harries, 57  
 Hartmuth, 194  
 Hassler, 219  
 Heat-insulating compositions, 346  
 Himicolloids, 77  
 Hemming, 340  
 Herzog, 43, 62, 108, 121, 128, 139  
 Hexatriene, 122  
 Hexenone, 167  
 Hosacus, 273  
 Houben, 70, 172  
 Hydrocarbon solvents, 6  
 Hydrogenation, 75
- INDENE, 92, 172, 251  
 Insulating material, 378  
 — properties, 267  
 Isomers, 42  
 Ivory, 334, 337
- JACOBSON, 55  
 Japan lac, 35, 38  
 John, 401

- KAHL, 144  
Katz, 113  
Kauri copals, 367  
Kentones, 65  
Ketene, 111  
Ketobutanol, 165  
Ketone-formaldehyde, 164  
Kieselguhr, 210, 315  
Kleeberg, 273  
Knauss, 190  
Knüppel, 240  
Krakan, 89  
Kraemer, 246  
Kreidl, 43, 62, 108, 121, 128, 139, 150  
Kronstein, 91  
Krumbhaar, 245  
  
LACCAIN, 283  
Lactic acid, 177  
Lactides, 34  
Lactones, 57  
Laminated products, 352  
Lamp shades, 360  
Lead oxide, 225  
Lebach, 10, 276  
Lenses, 408  
Ligroin, 167  
Lingner, 296  
Lignite tar, 380  
Linoleum, 7, 250  
—— cement, 269  
Linseed oil, 176, 201, 246, 381  
Liquid resins, 357  
Luft, 312  
Lyophilic colloids, 81  
Lyophobic phenomena, 77  
  
MAHDIHASSAN, 5  
Manilla copal, 360  
Mannite, 200  
Marbalith, 337  
Marcusson, 93, 237, 250  
Matrices for printing, 346  
Matthews, 88  
Mechanical strength, 41  
Meer, 273  
Meighan, 394  
Metastyrol, 89  
Melting point, 74, 388  
Meerschaum, 160  
Methylated products, 96  
Methyl ester, 120  
Methylolurea, 161  
Meunier, 189, 265  
Meyer, 55, 239  
Mica, 203  
  
Michael, 378  
Mikarta sheets, 268  
Mixibility, 39  
Möhlau, 215  
Molecular complexes, 43  
—— weight, 76  
Monoacetin, 321  
Morris, 93  
Motor-car parts, 345  
Moureu, 104  
“Mowilith” products, 101  
Mucilages, 18  
Müller, 166  
Mutual insolubility, 40  
Mylo, 149  
  
NAGEL, 57  
Naphthalene, 173, 202, 205  
Naphthol-formaldehyde resins, 295  
Natural resins, 30  
Negative catalysis, 73  
Nevadol, 372  
Neuss, 398  
Nitrile group, 68  
Novolak, 146, 151, 276, 304, 323  
Novonty, 336, 382  
  
OIL varnish, 247, 271  
Olein, 343  
Ormandy, 281  
Ott, 117  
Oxygen “bridges,” 56  
  
PALE resins, 322  
Pallaud, 386  
Parainolene, 241  
Para-indenes, 93  
Paraldehyde, 124  
Peralite, 355  
Peroxide complexes, 74  
Pertinax, 355  
Petroleum ether, 176  
Phenofom, 324  
Phenol-alcohols, 152  
Phenols, 9, 143, 181, 193, 217, 223, 331  
Phenoplast, 146  
Phenoplasts, 338  
Phenyl, 103  
Phenylbutadiene, 114  
Phosphoric acid, 175  
Photo-polymerization, 72  
Pickardt, 25  
Pigments, 343  
Pitches, 18, 315  
Plasticizing agents, 80, 358  
Plauson, 168, 190

- Pallak, 301, 320  
 Pollopos, 81, 139, 160  
 Polyglycollide, 57  
 Polymerization, 18, 47, 52  
     — by sunlight, 71  
 Press-mouldings, 339, 377  
 "Primary" resins, 15, 37  
 Printing ink, 249  
 Propenylbenzine, 94  
 Puchot, 185  
 Pummerer, 224  
 "Pyrido" rubber, 128  
  
**QUARTZ**, 358  
  
**RABINOVITZ**, 232  
 Raschig, 149  
 Refractive index, 337  
 Resenes, 32  
 Resinates, 158  
 Resin-forming condensation, 48  
 Resinoid amorphism, 21  
     — conditions, 39  
 Resinolic acid, 32  
 "Resinotannol resins," 34  
 "Resinomorphic" grouping, 44  
     — complex, 62  
     — soap, 262  
 "Resins," 29  
 Resistance to solvents, 55  
 Resite articles, 326  
 Resites, 146  
 Resitol, 146  
 Resoles, 324  
 Reynaud, 176  
 Rheiner, 116  
 Rhus vernicifera, 35  
 Ring formation, 58  
 Ripper, 399  
 Rohm, 99  
 Rosin soap, 249  
 Rubber, 315  
  
**SALICYLIC acid**, 144  
 Salinetines, 146, 328  
 Sandarac resins, 15  
 Saponifiable resins, 7  
 Sealing wax, 269  
 Scheiber, 19  
 Schneider, 240  
 "Schellan" solutions, 159, 396  
 Schultz, 67  
 "Secondary resin flow," 31  
 Seed disinfectants, 372  
 Shellac, 4, 11, 218, 283, 352  
     — substitutes, 114, 206, 275  
 Sibolite, 283  
  
 Silberrad, 128  
 Soapstone, 341  
 Solid monomers, 74  
 Sommerfield, 344  
 Space-lattice influences, 56  
 Spilker, 246  
 Spirit varnishes, 274  
 Stäger, 332  
 Stand oil, 248  
 Staudinger, 60, 73, 74  
 Stern, 244  
 Stilbene, 95, 107  
 Sticklac, 5  
 Stopping teeth, 296  
 Story, 307  
 Styrol, 79, 88, 234  
 Sulphocyanide, 177  
 Supercooled melt, 24  
 Sutherland, 203  
 Syneresis, 81  
 "Syntellac," 260  
  
**TAMMANN**, 24  
 Tar oils, 295  
 "Tarry products," 37  
 Tenacite, 347  
 Terpene mixture, 32  
 Terpenes, 31, 118  
 Tetraldan, 183  
 Textile finishes, 282, 373  
 Thermal tests, 412  
 Thiazol, 214  
 Thiocarbonyl group, 65  
 Tollens, 164  
 Tortoise-shell, 334, 337  
 Toron, 219  
 Trimerides, 124  
 Trolite, 347  
 Truxene, 92  
 Truxillic acids, 59  
 Tschirch, 13  
 Tubes, 352  
 Tung oil, 247  
 Turpentine, 3, 30, 213  
  
**ULTRAMICROCRYSTAL**, 27  
 Urushiol, 35, 46  
  
**VARNISH oil substitutes**, 246  
 Varnishes, 175, 211, 245  
 "Vectorial polymerization," 27  
 Vegetable secretions, 14  
 Vingtrie, 174  
 Vinylacetone, 106  
 Vinylacrylic acid, 63  
 Vinyl esters, 101  
 Viscosity, 75

- Vitreous condition, 30  
Volatility, 80  
Voorhout, 143  
Vulcanization of rubber, 159, 222  
"WACKER shellac," 260, 266  
Wall-paper printing, 269  
Waxed paper, 361  
Weimarm, 20, 21, 25  
Wendriner, 235  
Werner, 165  
Whitby, 93  
Wohl, 149, 167  
Wood tar, 296  
Wolff, 15, 243, 258  
Wright, 202  
XYLENE, 175, 304  
ZAPON varnish, 270  
Zimmermann, 204